

**State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD  
Stationary Source Division**

**STAFF REPORT: INITIAL STATEMENT OF REASONS**

**Public Hearing to Consider Amendments to the California Regulation  
Requiring Deposit Control Additives in Motor Vehicle Gasoline**

Date of Release: August 7, 1998  
Scheduled for Consideration: September 24, 1998

**Location:**

Kern County Board of Supervisors Office  
1115 Truxton Avenue  
Bakersfield, California 93301

This report has been reviewed by the staff of the Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. To obtain this document in an alternative format, please contact the Air Resources Board ADA Coordinator at (916) 322-4505, TDD (916) 324-9531, or (800) 700-8326 for TDD calls from outside the Sacramento area.

## **ACKNOWLEDGMENTS**

This report was prepared with the assistance and support from other divisions and offices of the Air Resources Board. We would like to acknowledge the invaluable participation and cooperative assistance that we received from many companies and organizations. In particular, we would like to thank Chevron USA, Oronite Chemical Co., Ford Motor Company, Texaco Additives International, Ethyl Corp., Lubrizol Corp., BASF Corp., Shell Research, Southwest Research Institute, E.G.&G Automotive Research, the American Automobile Manufacturing Association and the Coordinating Research Council for their comments and recommendations.

### **Principal Authors:**

Jim M. Aguila  
Linda Lee

### **Technical Editor**

Elizabeth Parkhurst

### **Contributing Staff:**

Faye Palmer  
Jacqueline Wilson

### **Reviewed and Approved By:**

Peter D. Venturini, Chief, Stationary Source Division  
Dean C. Simeroth, Chief, Criteria Pollutants Branch  
Gary M. Yee, Manager, Industrial Section

## TABLE OF CONTENTS

I.	INTRODUCTION AND SUMMARY	
A.	What Are the Current Requirements? . . . . .	1
B.	Why Are We Proposing Changes to the Gasoline Deposit Control Additive Regulation? . . . . .	2
C.	What Are We Proposing? . . . . .	2
D.	How Were the Proposals Developed? . . . . .	3
E.	What Are the Effects of the Proposed Changes? . . . . .	3
F.	What Are the Staff's Future Plans? . . . . .	4
II.	RECOMMENDATION . . . . .	5
III.	BACKGROUND	
A.	Evolution of Gasoline Deposit Control Additives . . . . .	6
B.	California Gasoline Deposit Control Additive Program . . . . .	6
C.	Federal Gasoline Deposit Control Additive Program . . . . .	7
IV.	PROPOSED AMENDMENTS	
A.	Intake Valve Deposit and Port Fuel Injector Deposit Performance Standards . . .	8
B.	Combustion Chamber Deposit Performance Standard . . . . .	8
C.	Certification Test Fuel Requirements . . . . .	9
D.	Eliminate Outdated Certifications . . . . .	9
E.	Test Methods . . . . .	10
V.	TECHNICAL DISCUSSION	
A.	Certification Performance Standards . . . . .	11
1.	Intake Valve Deposits . . . . .	11
2.	Port Fuel Injector Deposits . . . . .	12
B.	Combustion Chamber Deposit Performance Standard . . . . .	13
1.	The Role of Additives in Forming Combustion Chamber Deposits . . . . .	13
2.	Emission Reductions From Reduced Combustion Chamber Deposit Level .	15
C.	Certification Test Fuel Requirements . . . . .	17
1.	Specifications for Certification Test Gasolines . . . . .	17
2.	Certification Test Gasoline Blending Information . . . . .	17
D.	Test Methods . . . . .	18
VI.	FUTURE ACTIVITIES	

A.	Further Reductions in Combustion Chamber Deposits .....	20
B.	Consideration of Alternative Intake Valve Deposit Test Method .....	20
C.	Consideration of Alternative Combustion Chamber Deposit Compliance Options .....	21
D.	Coordination With the U.S. EPA .....	21
VII.	ENVIRONMENTAL AND ECONOMIC IMPACTS	
A.	Environmental Impacts .....	22
B.	Cost Impacts .....	22
C.	Small Business Impacts .....	23
D.	Global Warming and Ozone Depletion Impacts .....	23
REFERENCES		
APPENDICES		
A.	Proposed Regulation Order	
B.	Staff Evaluation of CCDs	
C.	NO <sub>x</sub> Benefit Calculation	
D.	ARB Vehicle Test Procedure for Evaluating IVDs and CCDs	
E.	CMA Petition and ARB Response	

## **I.**

### **INTRODUCTION AND SUMMARY**

This report is the Initial Statement of Reasons by the staff of the Air Resources Board (ARB or Board) to support the proposed amendments to the California Gasoline Deposit Control Additive Regulation (13 CCR, section 2257). The amendments will 1) update the existing performance standards for intake valves and port fuel injectors, 2) include a new combustion chamber deposit performance standard, 3) update the vehicle test methods, and 4) add clarity and specificity to the regulatory requirements. The proposed amendments will be considered at a Board hearing on September 24 or 25, 1998.

The gasoline deposit control additive regulation was adopted by the Board in 1990, and it was implemented in 1992. The regulation established a certification program in which gasoline marketers must demonstrate that their gasoline contains adequate levels of deposit control additives to effectively control intake valve and port fuel injector deposits. In 1996, the Board amended the regulation to update test methods, add compliance flexibility, and to clarify various regulation provisions.

#### **A. What Are the Current Requirements?**

The gasoline deposit control additive regulation requires that all commercial gasoline formulations be certified to contain effective levels of detergent additives. Under the current regulations, gasoline marketers are required to submit an application containing vehicle test results which show that their gasoline containing deposit control additives can 1) maintain low level of port fuel injector deposits, 2) effectively remove port fuel injector deposits, and 3) maintain low level of intake valve deposits. The three performance criteria were adopted by the Board to establish a rigorous performance evaluation to ensure that the California vehicle fleet is supplied with gasoline with effective deposit control additives. The ARB staff uses the information from the application and other information, as appropriate, to evaluate the application for certification. The staff has issued over 370 certifications.

The goal of the gasoline deposit control additive program is to remove the performance robbing effect of fuel system deposits, and thereby lower emissions. Both port fuel injector and intake valve deposits have been linked to excess vehicle emissions, due to their adverse effect on the engine combustion process. Control of excessive fuel

system deposits restores performance and allows vehicles to operate properly as designed.

## **B. Why Are We Proposing Changes to the Gasoline Deposit Control Additive Regulation?**

The staff believes that it is appropriate to update the existing gasoline deposit control additive regulation to take advantage of recent developments in additive chemistry and additive technology and changes to the use of additives resulting from the implementation of California's reformulated gasoline program (CaRFG), also known as Cleaner-burning gasoline.

Since the implementation of the gasoline deposit control additive regulation in 1992, deposit control additive chemistry has been continually improved to a point that current additives are highly optimized to control fuel system deposits while minimizing contributions to the formation of combustion chamber deposits. Both the fuel system deposits and combustion chamber deposits can adversely affect motor vehicle emissions. Studies have linked combustion chamber deposits to increased NO<sub>x</sub> emissions, thus reducing such deposits should result in reductions in NO<sub>x</sub> emissions.

In addition, the introduction of CaRFG in 1996 has resulted in commercial gasoline having less deposit forming tendencies than gasoline marketed prior to CaRFG. The combination of new technology additives and CaRFG have resulted in improved engine performance and emission benefits. At least one study showed about 30 percent less combustion chamber deposits with CaRFG relative to pre-CaRFG. This difference has been estimated by the staff to result in a reduction of vehicle NO<sub>x</sub> emissions by at least five percent. Therefore, we propose to cap existing combustion chamber deposit level to preserve this emission benefit.

The staff believes that it is also appropriate to update the program to recognize improved performance of additives to control fuel system deposits to a much lower level than currently required by the regulation. This would provide a better safeguard to ensure effective additives in the California gasoline market. Other updates and revisions are proposed to add clarity and specificity to the regulation and to make technical corrections in the referenced vehicle test methods.

## **C. What Are We Proposing?**

We propose the elimination of the port fuel injector deposit clean-up requirement and to make the existing intake valve deposit performance standard requirements more stringent in light of the improvements in the effectiveness of current additives. We also propose that a new performance standard for combustion chamber deposits be included which will require an

additional demonstration to obtain gasoline certification.

We also propose to preclude the use of outdated gasoline deposit control additive certifications which are based on old deposit control additive technology. This amendment will ensure the use of up-to-date additive packages are used in CaRFG.

We are proposing other amendments to further clarify and refine requirements on certification test gasolines. The proposed amendments provide additional guidance on test gasoline formulations and also will require applicants to submit information regarding the blend components used to make the certification test gasolines.

#### **D. How Were the Proposals Developed?**

In developing the proposed amendments, we conducted public workshops on March 24, June 11 and July 24, 1998, to discuss the latest research on combustion chamber deposits and development of the staff's proposals. We also held several meetings with individual additive, oil, and automobile companies, as well as various industry associations and other interested parties.

#### **E. What Are the Effects of the Proposed Changes?**

The proposed amendments will update our certification program for approving deposit control additives used in CaRFG. The proposed amendments will preclude any harmful effects from outdated deposit control additive packages and ensure that the existing level of fuel system deposits and combustion chamber deposits are not made worse.

The proposed amendments will preserve the emission benefits realized with the transition to CaRFG and current deposit control additive technology. The staff estimates that this emission benefit has resulted in reduced NO<sub>x</sub> emissions of at least five percent (about 50 tons per day) relative to the previous level within the California gasoline motor vehicle fleet. The proposed amendments will have no adverse environmental impact.

Other amendments to the certification performance standards and test gasoline criteria will update the program and add clarity and specificity to existing regulatory requirements. The proposed combustion chamber deposit test requirement will add minimal cost and eliminating the port fuel injector deposit clean-up test requirement will significantly reduce the cost of additive performance testing. Therefore, we expect a net reduction in the total cost of additive performance testing.

#### **F. What Are the Staff's Future Plans?**

The staff plans to continue investigating the potential for further emission benefits from combustion chamber deposit control below today's level. The staff also plans to evaluate an alternative vehicle test procedure for the intake valve performance standard and an alternative compliance option for the staff's proposed combustion chamber deposit performance standard. The staff will also coordinate with the U.S. EPA on their plans to evaluate combustion chamber deposits.



## **II.**

### **RECOMMENDATION**

We recommend that the Board adopt the proposed amendments to the regulation requiring deposit control additive use in California motor vehicle gasoline.

### **III.**

#### **BACKGROUND**

This chapter presents background information on the evolution of gasoline deposit control additives and the California and federal gasoline deposit control additive programs.

##### **A. Evolution of Gasoline Deposit Control Additives**

The use of additives in gasoline is not new. In the late 1960's, additives in gasoline were used mainly as carburetor anti-icing agents and corrosion inhibitors. From the late 1970's into the early 1990's, concerns over fuel quality were raised related to a fuels' tendency to create carburetor gumming, produce intake valve deposits, and plug port fuel injectors. Automakers indicated that fuel system deposits robbed vehicles of performance and would increase emissions. In response, gasoline marketers began to add deposit control additives to their gasolines to control fuel system deposits. Typically, these deposit control additives contained detergent additives, carrier fluids, and solvents. Water demulsifiers, corrosion inhibitors, and dyes were also included.

The active ingredients in deposit control additives are detergents, principally polyolefin amines (POA), polyisobutylene amines (PIBA), and polysuccinimides. Deposit control additive packages also contain carrier fluids which serve to transport detergent molecules to deposit and metal surfaces. Originally, additive manufacturers utilized petroleum mineral oils as carrier fluids. Today, additive packages contain optimized synthetic carrier fluids. Aromatic hydrocarbon solvents are also added to deposit control additive packages to fine tune viscosity requirements.

##### **B. California Gasoline Deposit Control Additive Program**

The ARB adopted the California gasoline deposit control additive regulation (title 13, California Code of Regulations, section 2257) in September of 1990, to ensure that all commercial motor vehicle gasolines contain effective deposit control additives.

The regulation established a certification program which requires that gasoline producers demonstrate that their gasoline containing deposit control additives:

- i) produce no more than an average of 100 mg/valve of intake valve deposits,

when tested in accordance with the ASTM D 5500-94 test method,

- ii) maintain low port fuel injector deposits such that port fuel injector deposits produce less than a 5% loss of flow of gasoline, when tested in accordance with the ASTM D 5598-94 test method, and
- iii) is able to remove deposits from plugged port fuel injectors to improve the flow loss from more than 10 percent plugging to no more than 5 percent plugging, when tested in accordance with the ARB's Test Method for evaluating Port Fuel Injector Deposits in Vehicle Engines, dated July 2, 1996.

The three performance criteria contained in the regulation, represent a rigorous additive performance demonstration to ensure that only effective additives are used in the California gasoline market. The performance demonstration was designed to be comprehensive since certification requires only a single pass of the intake valve deposit keep-clean, port fuel injector deposit clean-up, and port fuel injector deposit keep-clean tests. Also, these tests are conducted on one single engine type to show adequate additive deposit control effectiveness for the entire California vehicle fleet.

Since the gasoline deposit control additive regulation was implemented in January 1992, the ARB has certified over 370 gasoline formulations containing deposit control additives. Most of these gasoline certifications were issued for pre-CaRFG. Since the introduction of CaRFG, gasoline marketers have applied for new gasoline certifications to take advantage of the less deposit forming tendencies of CaRFG. Typically, CaRFG requires significantly less additives than pre-CaRFG to meet the performance tests of the regulation. Currently, all California gasoline marketers hold certifications based on CaRFG.

### **C. Federal Gasoline Deposit Control Additive Program**

In addition to the California gasoline deposit control additive regulation, the U.S. EPA also implemented a federal gasoline deposit control additive regulation in July 1997 that has limited application in California. Similar to the California program, the federal gasoline deposit control additive program requires similar demonstrations of intake valve deposit and port fuel injector deposit performance. However, the federal regulation does not require the port fuel injector deposit clean-up demonstration.

The U.S. EPA additive regulation considers California certification as equivalent to meeting the federal standards and exempts California gasoline marketers from obtaining federal certification, if they market entirely within California and they obtain California certification.

## **IV.**

## **PROPOSED AMENDMENTS**

This chapter provides a description of the proposed amendments to the gasoline deposit control additive regulation. This summary is intended to satisfy the requirements of Government Code section 11346.2(a)(1), which requires that a noncontrolling plain English summary of the regulations be made available to the public.

### **A. Intake Valve Deposit and Port Fuel Injector Deposit Performance Standards**

The staff is proposing to modify the current intake valve and port fuel injector deposit performance standards. One of the staff's proposals is to increase the stringency of the current intake valve deposit keep-clean pass/fail performance standard. The existing regulation requires that the test gasoline containing the deposit control additive produce less than a maximum average of 100 mg per valve. The staff proposes that the intake valve deposit keep-clean pass/fail performance standard be changed to a maximum average of 50 mg per valve.

The staff also proposes to eliminate the port fuel injector deposit clean-up test performance standard. This is to be in combination with the new lower intake valve deposit performance standard. No change is proposed for the existing port fuel injector deposit keep-clean standard.

### **B. Combustion Chamber Deposit Performance Standard**

The staff is proposing to add a new combustion chamber deposit performance standard to the existing requirements for certification of gasolines with deposit control additives. The proposed performance standard for combustion chamber deposits is to ensure that the use of deposit control additives will not result in higher levels of combustion chamber deposits in the California vehicle fleet.

Specifically, the staff is proposing the establishment of a maximum average combustion chamber deposit performance standard of 1300 mg/cyl (averaged across four cylinders), when tested with the new proposed ARB vehicle combustion chamber deposit test method (Appendix D). The staff is also proposing an optional combustion chamber deposit performance standard in which applicants may show that their gasoline containing a deposit control additive will not produce more than 140 percent of the combustion chamber deposits formed relative to their gasoline containing no deposit control additive. (Appendix B contains a detailed discussion on how the proposed combustion chamber deposit standard was derived.)

### **C. Certification Test Fuel Requirements**

The staff proposes to specify a T90 distillation temperature for test gasoline used for certification. Specifically, the T90 distillation temperature of the certification test gasolines would be required to be within 40 °F of the maximum requested cap limit for T90. (Typical T90 temperatures are from 290 to 330 °F.)

In addition, the staff proposes that applicants be required to provide information on the blend stocks used to produce the certification test gasoline. The proposed amendments would allow the staff to request more detailed information about the blend stock components to determine the representativeness of the certification test gasoline, as compared to the typical gasoline to be marketed under an issued certification. This information is to help ensure that the gasoline used in the certification test fuels are representative of real world California gasolines and that additives will be effective.

### **D. Eliminate Outdated Certifications**

The staff is proposing that outdated gasoline certifications which were issued prior to July 1, 1996 be voided. These certifications are based on outdated additive technology that are rarely used, and the additives, while effective in controlling fuel system deposits, have a high potential to form combustion chamber deposits.

The staff also proposes that gasoline certifications granted between July 1, 1996, and 30 days after the effective date of these proposed amendments be allowed to be used. Under the staff's proposal, these gasoline certifications will not have to provide a combustion chamber deposit demonstration. The 30 day period is provided to allow a transition to the new proposed amendments to account for ARB's review of new certification applications. The staff's evaluation of the information supporting these certifications indicate that these should not pose a significant potential to adversely impact combustion chamber deposits. For gasoline certification applications submitted after implementation of the proposed amendments, applicants will be required to submit data showing compliance with all the amended and existing certification criteria, including a demonstration for acceptable combustion chamber deposit performance.

### **E. Test Methods**

The staff proposes that section 2257(c)(1)(A)(I), the referenced intake valve deposit test method (ASTM D 5500-94), be updated to incorporate the latest version of the ASTM intake valve deposit test method. The staff also proposes that section 2257(c)(1)(A)(ii) be

amended to update the referenced port fuel injector test method (ASTM D 5598-94) with the latest version of that test method, ASTM 5598-95a. Finally, the staff proposes an amendment to 2257(c)(1)(A)(iii) to include a new vehicle test method for determining combustion chamber deposits for the proposed new combustion chamber deposit performance standard.

The proposed amendments incorporate by reference published ASTM test methods. Copies of these test methods can be obtained from ASTM at 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, telephone number (610) 832-9585, and facsimile number (610) 832-9555.

## **V.**

### **TECHNICAL DISCUSSION**

This chapter includes a discussion of the technical basis for the proposed amendments to the gasoline deposit control additive regulation.

#### **A. Certification Performance Standards**

##### *1. Intake Valve Deposits*

As discussed in Chapter IV, the staff is proposing that the current intake valve deposit keep-clean standard be lowered to 50 mg/valve. The basis for this proposal stems from a review of recent gasoline certification applications which indicate that the existing intake valve deposit standard does not guarantee that the more improved and effective deposit control additive technology will be used.

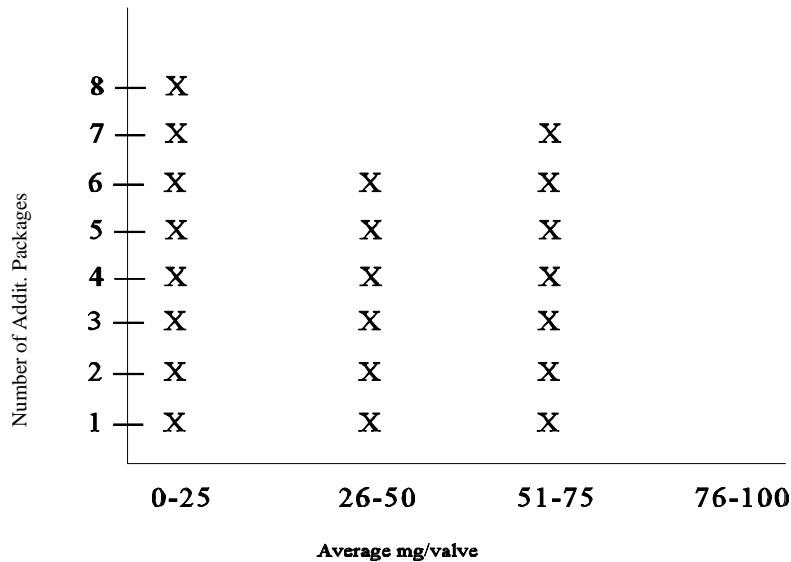
Figure V-1, shows individual intake valve deposit test data results for deposit control additive packages contained in gasoline formulations which were certified between July 1996 and June of 1998. As indicated, these additive packages have resulted in consistently low intake valve deposit test results in comparison to the 100 mg/valve standard in the regulation. As shown, 14 of the total 21 approved and certified gasoline formulations containing these additive packages resulted in intake valve deposit levels below 50 mg/valve. At this time, the major refiners and pipeline distribution companies that add deposit control additives to gasoline marketed in California have gasoline certifications using at least one of the additive packages meeting an intake valve deposit level below 50 mg/valve.

Based on discussions with additive manufacturers, the staff believes that consistently low intake valve deposit test results are an indication that current deposit control additive packages are sophisticated enough to address deposit formation in all areas of an engine.

The staff also believes that additives with lower demonstrated intake valve deposit level will likely provide better control of deposits within the California vehicle fleet. Industry acknowledges that some vehicles exist in the California fleet that produce a higher intake valve deposit level than the referenced 1.8L BMW test vehicle currently used for official intake valve deposit measurement. Thus, any incremental downward change in intake valve deposits results from the BMW test vehicle will translate into larger downward differences for vehicles which form more intake valve deposits than the BMW engine. Some studies also

suggest that emission benefits may be associated with lower intake valve deposit levels. However, further research is required to fully determine the emission effect of incremental intake valve deposit removal.

**Figure V-1**  
**Certification Intake Valve Deposit Test Performance Results**  
**1996-1998**



## 2. *Port Fuel Injector Deposits*

Earlier this year, the Chemical Manufacturers Association (CMA) requested the ARB to rescind the port fuel injector clean-up performance demonstration requirement from the regulation. The CMA indicated that the requirement was unnecessary and not cost-effective. The staff denied the petition indicating that repeal of the port fuel injector deposit clean-up requirement would constitute a significant relaxation of the performance criteria which currently ensures effective deposit control additives for all California vehicles. In the response, the staff also indicated their desire to continue the dialog with CMA in the context of the current rulemaking effort. (A copy of the CMA petition and the ARB response is contained in Appendix E.)

A review of issued gasoline certifications show that certifications that have excellent intake valve deposit performance below 50 mg/valve also consistently demonstrated excellent PFI deposit removal. The staff believes that a more stringent intake valve deposit standard such as the staff's proposal, would provide additional assurance for effective deposit control additives and would, therefore, eliminate the need for the port fuel injector deposit clean-up demonstration. Thus, the staff proposes to eliminate the port fuel injector deposit clean-up



requirement.

## **B. Combustion Chamber Deposit Performance Standard**

Over the last year, the staff has been investigating the role of combustion chamber deposits on emissions. As part of our discussions with the automobile manufacturers and oil companies, the staff found that the combustion chamber deposit level in today's California vehicle fleet has substantially dropped since the introduction of CaRFG. The staff found that the reduction in the combustion chamber deposit level was mainly due to improved additive technology and a reduction in the deposit-forming potential of CaRFG. CaRFG has a lower aromatic hydrocarbon content and lower T90 distillation temperature, which results in lower combustion chamber deposits.

### *1. The Role of Additives in Forming Combustion Chamber Deposits*

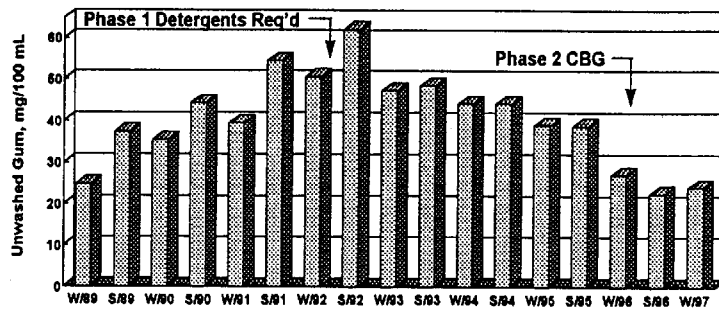
Improvements in additive technology have evolved from controlling deposits in the vehicle fuel systems, to controlling deposits both in the vehicle fuel system and the engine combustion chamber. In November 1993, the Coordinating Research Council (CRC), an organization representing the research interests of automobile and oil industries, conducted a workshop to evaluate concerns over combustion chamber deposits. At the workshop, the Chrysler Corporation and other automobile manufacturers shared the results of their studies which found that some engine designs were sensitive to combustion chamber deposit formation and led to a condition, known as "carbon rap", where deposits on the piston top and cylinder head would cause the piston head to rock at top dead center, and thereby cause a knocking sound. Researchers soon found that combustion chamber deposits were the cause of carbon rap. They also concluded that due to federal and California mandates requiring additive use, the concentrations of additives in gasoline dramatically increased which was suspected of contributing to the increased formation of combustion chamber deposits.

Figure V-2 shows that California gasoline unwashed gum level rose dramatically during the early 1990's, coinciding with the implementation of the California gasoline deposit control additive regulation. The industry routinely uses unwashed gum measurements to determine the overall amount of additives in a base gasoline and is an indicator of the gasoline's potential to form deposits. The peak in gasoline unwashed gum level occurred during the summer of 1992, which also coincides with Chrysler's reports of carbon rap.

Subsequent studies have confirmed that deposit control additives contribute to the formation of combustion chamber deposits. Studies on commercial gasolines indicate that the use of deposit control additives can contribute to combustion chamber deposit formation by 20 to 40 percent above unadditized base gasolines. The range is somewhat indicative of

the variation in additive technologies and their effectiveness. Modern additives require lower dosage rates, which lessens the potential to form combustion chamber deposits. Also, optimized additive chemical components are less prone to combustion chamber deposit formation. Ineffective older technology additives require higher dosage rates and are prone to increasing combustion chamber deposits.

**Figure V-2**  
Unwashed Gum- AAMA National Survey  
Premium Gasoline- SF and LA Sample Average



Source: Oroville Presentation at 3/24/98 ARB Workshop

To address concerns of combustion chamber deposits and other market demands, additive manufacturers have significantly reformulated their deposit control additive packages over the last several years. Table V-1 shows a comparison of deposit control additive packages which were approved for use in California gasoline in 1992 and 1996. As indicated, in 1992 deposit control additive packages consisted mainly of less effective polyolefin amine (POA) detergents and used mineral oil based carrier fluids. These deposit control additive packages typically required much higher dosage rates to meet the certification performance standards. The staff found that in 1992, commercial gasoline contained an average dosage rate of 279 pounds of deposit control additive per thousand barrels of gasoline (ptb). Research indicates that both the use of mineral oil carrier fluids and high dosage rates contribute to increased combustion chamber deposit formation.

By 1996, most additive packages consisted of synthetic carrier fluids which were optimized to contribute less to combustion chamber deposits. Detergent additives were also developed to be significantly improved and resulted in new polyisobutylene and polyether amine detergents. Deposit control additives had evolved to a point that, by 1996, the average deposit control additive dosage rate had been reduced to 127 ptb to meet the certification performance standards. The combination of improved additive chemistry

and reduced dosage rates has resulted in reductions in combustion chamber deposit formation.

**Table V-1**  
Comparison of Deposit Control Additive Packages

Addit. Pkg.	1992		Addit. Pkg.	1996	
	Detergent <sup>a/</sup>	Carrier		Detergent <sup>a/</sup>	Carrier
A	POA	Mineral Oil	I	POA	Mineral Oil
B	PEA	none	J	PIBA	Mineral Oil
C	PIBA	Synthetic	K	PEA	Synthetic
D	POA	Mineral Oil	L	PEA/PIBA	Synthetic
E	PIBA/PES	Mineral Oil	M	PIBA	Synthetic
F	POA	Mineral Oil	N	PEA/POA	none
G	POA	Mineral Oil	O	PEA	none
H	POA	Mineral Oil	P	PIBA	Synthetic

<sup>a/</sup> POA- Polyolefin Amine; PEA- Polyether Amine; PIBA- Polyisobutylene Amine  
PES- Polyether Succinimide;

The reformulation of commercial gasoline under the CaRFG regulations is another significant reason for the lower California vehicle fleet combustion chamber deposit level. Basic research concludes that combustion chamber deposits form from the heavy hydrocarbon molecules. These are found in the aromatic hydrocarbon, olefin, and T90 portions of the gasoline. Under the CaRFG regulations, the level of these has been significantly reduced. Based on the findings of one Texaco study, reducing aromatics from 32 to 23 volume percent could result in about a 23 percent reduction in combustion chamber deposit thickness (see Appendix B, Figure B-1). Appendix B contains a detailed discussion of the fuel effects on combustion chamber deposit formation.

## 2. *Emission Reductions From Reduced Combustion Chamber Deposit Level*

A major benefit of reduced combustion chamber deposit level is a reduction in NO<sub>x</sub> emissions. Although only limited studies have determined the emission benefits of partial combustion chamber deposit removal, several studies have confirmed the NO<sub>x</sub> benefit when combustion chamber deposits are completely removed from a dirty engine. This is most evident in the CRC study that indicated a 19.6 percent NO<sub>x</sub> increase due to combustion chamber deposits. Table V-2 shows a summary of results from several studies. Based on a review of these studies, the staff estimates that the reduced combustion chamber deposit level achieved from new technology additives, in combination with CaRFG, has resulted in at least a five percent reduction in vehicle NO<sub>x</sub> emissions, about 50 tons per day in 1996 (see

Appendix C for a full discussion).

**Table V-2**  
Summary of Combustion Chamber Deposit  
Clean-up Studies

<b><u>Company</u></b>	<b><u>NOx Reduction</u></b>	<b><u>Source</u></b>
Texaco	12-39%	SAE 940345
Penn State	30%	SAE 950740
Oronite	15-55%	company study
Shell	25%	SAE 962027
Toyota	20%	SAE 941893
CRC Study	19.6%	industry study
Nippon Oil	30%	SAE 971721

In general, the staff and industry agree that California has realized a significant NO<sub>x</sub> benefit from the reduced combustion chamber deposit level in California and that the NO<sub>x</sub> benefit should be preserved. In considering how best to preserve the benefit, staff determined that capping the existing level of combustion chamber deposits would be the most appropriate method. In reviewing vehicle test data, staff found that the maximum combustion chamber deposit level associated with CaRFG is approximately 1300 mg/cylinder, including the contribution from deposit control additives. (A detailed discussion is provided in Appendix B.)

Also, to further preserve the NO<sub>x</sub> benefit, staff determined that additives that are prone to forming combustion chamber deposits should not be allowed. In reviewing gasoline certifications approved prior to July 1, 1996, the staff found that these certifications typically used mineral oil carriers and less effective detergents. These outdated additives required higher dosage rates to meet the certification performance standards and contribute to increased combustion chamber deposit formation. Also, the staff found that these outdated certifications are rarely used and that gasoline marketers have newer replacement gasoline certifications.

## **C. Certification Test Fuel Requirements**

### *1. Specifications for Certification Test Gasolines*

Under the current regulatory criteria, certification test gasolines are required to be within 80 percent of the maximum requested properties for aromatic hydrocarbon content, olefin content, sulfur content, and oxygen content. However, the current criteria in the gasoline deposit control additive regulation does not specify a T90 distillation temperature. Therefore, the staff has determined that a specific T90 distillation temperature should be contained in the regulation to ensure that certification test gasolines represent commercial gasolines.

In reviewing prior certifications on CaRFG, the staff has found T90 distillation temperature of the certification test gasolines to be as low as 40 °F below the existing CaRFG cap limit for T90 distillation temperature. For example, certifications requesting the maximum limit for CaRFG T90 distillation temperature of 330 °F typically formulate certification test gasolines to contain a T90 distillation temperature of at least 290 °F. Therefore, the staff has determined that a T90 distillation temperature should be specified to be within 40 °F of the applicant's requested maximum for T90 distillation temperature.

### *2. Certification Test Gasoline Blending Information*

Some individuals have commented that there may be a potential to “tailor” a certification test fuel to limit its intake valve deposit and combustion chamber deposit forming characteristics through the use of specialized blend stocks. This practice would likely require less additive dosage that would normally be required to meet the certification performance standards.

To address this concern, the staff has determined that more specific information is needed that is related to the blending of the certification test gasoline and how it compares to typical California refinery blend stocks. The information should include a list of the refinery blend stocks used to blend the certification test gasoline, as well as, a list of the applicant's typical refinery blend stocks used to produce CaRFG. It may also be necessary to request certification test gasoline blend stock property data for aromatics, olefins, sulfur, oxygen content, and T90, to make a more detailed comparison.

Table V-3 below provides an example of the blend stock information that would be required for applications requesting certification to the CaRFG cap limits. Essentially, applicants are to show that the blend stock profile of their certification test gasoline will be in the expected range of blend stock composition for their typical CaRFG gasoline. The expected range of blend stocks used for production of an average CaRFG are shown on Table V-3. If an application requests certification to property levels higher than the CaRFG cap limits, then the applicant would need to show the expected blend stock profile

for the gasoline to be produced under the certification for comparison purposes.

The staff believes that by requiring the certification test gasoline blend stock data, greater control may be exercised to identify inappropriate blending components that may be added to “tailor” the certification test gasoline.

**Table V-3**  
Sample of Data to be Submitted for Certification Test  
Gasoline Compared to Avg. CaRFG Properties

Certification Gasoline		Average CaRFG <sup>a/</sup>	
<b>Blend Stock Component</b>	<b>Range</b>	<b>Blend Stock Component</b>	<b>Range</b>
Reformat, vol%	report	Reformat, vol%	20 to 30
MTBE., vol%	report	MTBE, vol%	10.8 to 11.2
Cracked stocks, vol% <sup>b/</sup>	report	Cracked stocks, vol% <sup>b/</sup>	20 to 35
Alkylate, vol%	report	Alkylate, vol%	15 to 20
Isomate, vol%	report	Isomate, vol%	2 to 10
Straight run naphtha, vol%	report	Straight run naphtha, vol%	as needed
Other (e.g. butane)	report	Other (e.g. butane)	as needed

<sup>a/</sup> Source: *CaRFG Performance and Compatibility Test Program Report*, March 1996.

<sup>b/</sup>FCC & hydrocracked streams

#### **D. Test Methods**

The gasoline deposit control additive regulation currently references test procedures for the PFI keep-clean and intake valve deposit keep-clean tests. The PFI keep-clean test, American Society for Testing and Materials (ASTM) D5598-94, requires the operation of a four cylinder, 2.2 liter, turbocharged, PFI Chrysler engine over a predetermined cycle while using the additized gasoline formulation. Additive effectiveness is measured by the percent fuel flow plugging of fuel injectors after the test cycle.

The regulations also reference ASTM D5500-94. This test is based on the Barvarian Motor Works (BMW) 10,000 mile intake valve deposit test procedure, which is used to evaluate additive performance on intake valves. This industry test method uses a 318i BMW, PFI, 4-cylinder vehicle with new intake valves. The vehicle is driven on a predetermined driving cycle while using the additized gasoline formulation. Additive effectiveness is measured as the weight of the deposits which form on the intake valves after mileage accumulation.

Since the staff last updated the test procedures in 1996, the ASTM has published updated procedures for PFI keep clean (ASTM D 5598-95a) and will soon publish new procedures for intake valve keep-clean (ASTM D 5500-98) testing. The updated ASTM test methods are based on the test procedures referenced in the regulation but include more detailed procedural instructions and address technical issues with the tests. The updated ASTM test methods are improvements over the current test methods and should serve to reduce test variability caused by procedural inconsistencies. The U.S. EPA has also addressed these procedural issues and provided informal guidance in their response in the 1996 Summary of Questions and Answers.

Presently, there is no reference test method for evaluating combustion chamber deposits. However, as discussed earlier, several studies have been conducted to evaluate combustion chamber deposits and in this effort standardized procedures have been developed. Both EG&G Automotive Research and Southwest Research Institute have extensive experience in conducting tests for combustion chamber deposits and have developed separate, but conceptually similar, test procedures.

Generally, these test procedures are an add-on test procedure to the existing intake valve deposit procedure, such as ASTM D5500-98 (BMW intake valve deposit keep-clean test). After mileage accumulation, the cylinder head is removed and the combustion chamber deposits are scraped off the piston tops, cylinder head, and combustion chamber surfaces of the intake valves. The deposits are then carefully collected and weighed. After removal of the combustion chamber deposits, intake valve deposits, if measured, are measured according to the intake valve deposit test procedure. The staff's proposed combustion chamber deposit test procedure in Appendix D is based on these two procedures.

## **VI.**

### **FUTURE ACTIVITIES**

This chapter discusses future activities that will be conducted to ensure that the gasoline deposit control additive regulation is kept up-to-date.

#### **A. Further Reductions in Combustion Chamber Deposits**

As previously discussed, the proposed amendments for combustion chamber deposits will preclude an increase in the existing combustion chamber deposit level in the future. This will preserve the emission benefits associated with the reduced level of combustion chamber deposits as a result of CaRFG and new technology additives. However, some data suggest that incremental reductions in combustion chamber deposits may provide further vehicle performance and emission benefits. Therefore, the staff plans to continue evaluating the potential for further benefits from combustion chamber deposit control, relative to today's level.

The CRC plans to conduct a two part study to define the incremental combustion chamber deposit/NO<sub>x</sub> emission correlation and to develop a uniform test method for combustion chamber deposits which will accurately rank additive performance in a repeatable fashion. The combustion chamber deposit emission study will also be followed up with a validation study to compare test results to the "real world" national average deposit level. We plan to follow this study, as well as other industry studies. If further benefits from combustion chamber deposit control are justified, then the staff will propose appropriate amendments to the gasoline deposit control additive regulation.

#### **B. Consideration of Alternative Intake Valve Deposit Test Method**

The ASTM has recently developed a new engine dynamometer test procedure, based on the Ford 2.3 liter engine, to measure intake valve deposits. Recent studies have shown that the new test procedure has much less variability than the current intake valve deposits test procedure required in the regulation. The staff intends to evaluate the new test procedure, in coordination with the U.S. EPA. If data supports use of the test method, then the staff will recognize the new test method as an equivalent test method for intake valve deposit performance demonstrations.



### **C. Consideration of Alternative Combustion Chamber Deposit Compliance Options**

While the proposed combustion chamber deposit demonstration requires minimal effort and expense, the staff recognizes other alternative ways in which combustion chamber deposit control may be demonstrated. One such alternative that may be more cost-effective is a thermogravimetric analysis (TGA) procedure which is currently being used to evaluate thermal stability of gasoline formulations and deposit control additive packages. The automotive industry has produced data showing that there may be a good correlation between gasoline washed gum TGA results and combustion chamber deposit amounts. Industry is currently evaluating this alternative procedure and will be developing a data base to determine if a correlation exists. The staff will be following the developments of this effort.

### **D. Coordination With the U.S. EPA**

During the development of the federal final rule on gasoline additives, the U.S. EPA also showed an interest in regulating combustion chamber deposits. However, at that time, insufficient data were available to develop a regulation. Since then, the U.S. EPA has expressed new interest in evaluating combustion chamber deposits and their effects on octane requirement increase. The staff plans to continue to work with the U.S. EPA to ensure coordination of the federal and California gasoline deposit control additive programs.

## **VII.**

### **ENVIRONMENTAL AND ECONOMIC IMPACTS**

This chapter summarizes the environmental and economic impacts associated with the proposed amendments to the gasoline deposit control additive regulation.

#### **A. Environmental Impacts**

The proposed amendments are intended to preserve the emission benefits resulting from improvements in gasoline deposit control additive technology and combustion chamber deposit benefits from CaRFG. Requiring a lower intake valve deposit standard will provide added assurance that California commercial gasoline will contain effective deposit control additives. Effective deposit control additives are known to minimize fuel system deposits and reduce motor vehicle emissions. The addition of a combustion chamber deposit performance requirement, with the invalidation of older gasoline certifications, ensures that current and future use of deposit control additives will not increase combustion chamber deposits from the existing level. These provisions will help maintain the emission benefits already gained from the use of CaRFG and current technology additives.

The proposed changes in the certification test gasoline requirements will help ensure that the certification test gasoline represents commercial gasoline. The proposal requiring the submittal of blend stock composition of the certification test gasoline and of the commercial gasoline will ensure that the certification test gasoline falls within the range of commercial formulations. These requirements will minimize the use of less effective deposit control additive packages in the gasoline market place.

Also, deleting the port fuel injector deposit clean-up provisions, in conjunction with making the intake valve provisions more stringent, will not result in any adverse environmental impact.

#### **B. Cost Impacts**

In general, the proposed amendments should not affect the overall cost of gasoline marketers to comply with the gasoline deposit control additive regulation. The staff's proposal to eliminate the port fuel injector deposit clean-up test requirement and to include the new combustion chamber deposit performance test will affect the cost of demonstrating

the additive effectiveness in gasoline. We expect that a significant savings should occur due to the elimination of the port fuel injector deposit clean-up test, which is estimated at a typical cost of about \$10,000. Likewise, the cost of the new combustion chamber deposit test procedure should only increase the cost of testing by about \$500, because the combustion chamber deposit measurement would be made during the required intake valve deposit performance test run.

**C. Small Business Impacts**

The Government Code requires the ARB to discuss how complying with a proposed regulation could adversely affect small businesses. (Small businesses are defined by Government Code Section 11342 *et seq.*) We believe that adoption of the proposal should not result in any significant adverse impacts on small businesses.

**D. Global Warming and Ozone Depletion Impacts**

The proposed amendments for the gasoline deposit control additive certification program are not expected to increase emissions of greenhouse gases that may contribute to global warming or pollutants that may contribute to stratospheric ozone depletion.

## REFERENCES

1. Barnes, J. R., Stephenson, T., *Influence of Combustion Chamber Deposits on Vehicle Performance and Tailpipe Emissions*, Society of Automotive Engineers (SAE) Technical Paper Series no. 962027.
2. Bitting, W. H., Firmstone, G. P., Keller, C. T., *Effects of Combustion Chamber Deposits on Tailpipe Emissions*, SAE Technical Paper Series no. 940345.
3. Cheng, Shi-wai Steve, *A Micrographics Study of Deposit Formation Processes in a Combustion Chamber*, SAE Technical Paper Series no. 962008.
4. Cheng, Shi-wai Steve, *The Effects of Engine Oils on Intake Valve Deposits and Combustion Chamber Deposits*, SAE Technical Paper Series no. 932810.
5. Choate, P. J., and Edwards, J. C., *Relationship Between Combustion Chamber Deposits, Fuel Composition, and Combustion Chamber Deposit Structure*, SAE Technical Paper Series no. 932812.
6. Clarke, L. J., Haddock, G. J., *The Relationship Between Gasoline Additive Thermal Stability and Combustion Chamber Deposits*, Pamphlet, Society of Automotive Engineers, Inc, 1997.
7. Coordinating Research Council, Inc., *Literature Search on the Impact of Combustion Chamber Deposits on Engine Performance*, CRC Project No. CM-136-950, August 1995.
8. Coordinating Research Council, Inc., *Proceedings of the CAC Workshop on Combustion Chamber Deposits*, held at Sonesta Villas Orlando, Florida, November 15-17, 1993.
9. Corkwell, K. C., Megnin, M. K., *Fleet Test Evaluation of Gasoline Additives for Intake Valve and Combustion Chamber Deposit Clean up*, SAE Technical Paper Series no. 950742.
10. Corkwell, K. C., Firmstone, G. P., *Repeatability of Intake Valve Deposit Measurements in the CRC 2.3L Ford Intake Valve Deposit Dynamometer Test*, SAE Technical Paper Series no. 962011.
11. Crema, S., Schreyer, P., Miln, T., *Effect of Thermal Stability of Detergents and Carrier Fluids on the Formation of Combustion Chamber Deposits*, SAE Technical Paper Series no. 961097.

12. Daly, D. T., Bannon, S. A., Fog, D. A., Harold, S. M., Mechanism of Combustion Chamber Deposit Formation, SAE Technical Paper Series no. 941889.
13. Daly, D. T., Dohner, B. R., The Rate and Characterization of Combustion Chamber Deposit Formation in a 2.3L Ford Engine, Symposium on the Mechanism for Combustion Chamber Deposits, March, 24, 1996.
14. Harpster, H. O., Matas, S. E., Frey, J. H., Litzinger, T. A., An Experimental Study of Fuel Composition and Combustion Chamber Deposit Effects on Emissions from a Spark Ignition Engine, SAE Technical Paper Series no. 950740.
15. Houser, H. K., Crosby, T. A., The Impact of Intake Valve Deposits on Exhaust Emissions, SAE Technical Paper Series no. 922259.
16. Kalghatgi, G. T., Combustion Chamber Deposits in Spark-Ignition Engines - A Literature Review, SAE Technical Paper Series no. 952443.
17. Kalghatgi, G. T., Deposits in Gasoline Engines - A Literature Review, SAE Technical Paper Series no. 902105.
18. Kalghatgi, Gautam T., Fuel and Additive Effects on the Rates of Growth of Combustion Chamber Deposits in a Spark Ignition Engine, SAE Technical Paper Series no. 972841.
19. Kalghatgi, Gautam T., Combustion Chamber Deposits and Knock in a Spark Ignition Engine - Some Additive and Fuel Effects, SAE Technical Paper Series no. 962009.
20. Kalghatgi, Gautam T., Effects of Combustion Chamber Deposits, Compression Ratio and Combustion Design on Power and Emissions in Spark-Ignition Engines, SAE Technical Paper Series no. 972886.
21. Megnin, M. K., Choate, P. J., Combustion Chamber Deposit Measurement Techniques, SAE Technical Paper Series no. 940346.
22. Moore, S., M., Combustion Chamber Deposit Interference Effects in Late Model Vehicles, SAE Technical Paper Series no. 940385.
23. Nagao, M., Kaneko, T., and Omata, T., Iwamoto, S., Ohmori, H., Matsuno, S., Mechanism of Combustion Chamber Deposit Interference and Effects of Gasoline Additives on CCD Formation, SAE Technical Paper Series No. 950741.
24. Nikanjam, M., Doom, R., The Effects of Fuels and Engines on Intake Valve and Combustion Chamber Deposits, SAE Technical Paper Series no 962028.

25. Omata, T., Hamatani, K., Kaneko, T., Yoshil, T., Nagao, M., Analytical Studies of Combustion Chamber Deposits and Effects of CCDs on Emissions, Pamphlet, Society of Automotive Engineers, Inc, 1997.
26. Papachristos, M., Raath, A., Trainor, M., Effects of Gasoline Detergent Additives on Formation of Intake Valve and Combustion Chamber Deposits, S.I.A. 94.09.26.
27. Price, R. J., Beck, C. M., C. D., Morley, C., Some Evidence for Chemical Effects on Octane Requirement Increase from Deposits in Spark Ignition Engines, SAE Technical Paper Series no. 971668.
28. Price, R. J., Spink, C. D., Morley, C., Prediction of Combustion Chamber Deposit Growth in SI Engines, SAE Technical Paper Series no. 972835.
29. Price, R. J., Wilkinson, P. T., Jones, D. A. J., Morley, C., A Laboratory Simulation and Mechanism for the Fuel Dependence of SI Combustion Chamber Deposit Formation, SAE Technical Paper Series no. 952445.
30. Richardson, C. E., Fischer, J. L., Pawczuk, G., Evaluation of the Effect of Fuel Composition and Gasoline Additives on Combustion Chamber Deposits, SAE Technical Paper Series no. 962012.
31. Shibata, G., Nagaishi, H., Oda, K., Effect of Intake Valve Deposits and Gasoline Composition on SI Engine Performance, SAE Technical Paper Series no. 922263.
32. Takei, Y., Uehara, T., Hoshi, H., Okada, M., Effects of Gasoline and Gasoline Detergents on Combustion Chamber Deposit Formation, SAE Technical Paper Series no. 941893.
33. Uehara, T., Takei, Y., Hoshi, H., Shiratani, K., Okada, M., Study on Combustion Chamber Deposit Formation Mechanism - Influence of Fuel Components and Gasoline Detergents, SAE Technical Paper Series no. 971722.
34. Zahalka, T. L., Kulinowski, A. M., Malfer D. D., A Fleet Evaluation of IVD and CCD: Emissions Effects and Correlation to the BMW 318i and Ford 2.3L IVD Test, SAE Technical Paper Series no. 952447.

## APPENDIX A

### **PROPOSED REGULATION ORDER**

## PROPOSED REGULATION ORDER

Note: The proposed amendments are shown in *italics* to denote regulation text additions and ~~strikeout~~ to show regulation text deletions.

### § 2257. Required Additives in Gasoline.

(a) Regulatory Standard.

(1) On or after January 1, 1992, no person shall sell, offer for sale, supply, or offer for supply any California gasoline unless at the time of the transaction:

[i] the producer, importer, or distributor of the gasoline has been issued a currently effective certification *for California gasoline* pursuant to subsection (c), *dated no earlier than July 1, 1996. Existing certifications dated between July 1, 1996 and (insert date 30 days after the effective date of the amendments)* that meet the requirements of subsection (c)(1)(A)(i) and (c)(1)(A)(ii) are exempted from subsection (c)(1)(A)(iii), and

[ii] the gasoline contains at least the minimum concentration of the additive or additives identified in the final application for certification.

(2) Subsection (a)(1) shall not apply to transactions where the person selling, supplying, or offering the gasoline demonstrates that:

[i] the gasoline has not yet been sold, offered, or supplied from the final distribution facility, and either

[ii] the person has taken reasonably prudent precautions to assure that he or she will bring the gasoline into satisfaction with the requirements of subsection (a)(1) before it is sold, supplied or offered from the final distribution facility, or

[iii] at or before the time of the transaction the person has obtained a written statement from the purchaser, recipient, or offeree of the gasoline stating that he or she is a distributor who has been issued a currently effective certification pursuant to subsection (c), and will cause the gasoline to satisfy the requirements of subsection (a)(1) before it is sold, supplied or offered from the final distribution facility.

(3) Subsection (a)(1)[ii] shall not apply to the sale, supply, or offer of gasoline from a final distribution facility where the person selling, supplying, or offering the gasoline demonstrates that the gasoline will be corrected to comply with section (a)(1)[ii] prior to the sale of gasoline from the retail outlet to be dispensed into motor vehicles. If such corrective action is taken, the producer, importer, or distributor of the gasoline must notify the Compliance Division of the Air Resources Board by telephone or in writing within 2 business days of the correction and must maintain records to document each occurrence in accordance with subsection (d).

(4) For the purposes of subsection (a)(1), each sale of gasoline at retail for use in a motor vehicle, and each supply of gasoline into a motor vehicle fuel tank, shall also be deemed a sale or supply by any person who previously sold or supplied such gasoline in violation of subsection (a)(1).



(b) Definitions.

For the purposes of this section:

(1) "Additive" means any substance or mixture of substances that is intentionally added to gasoline for the purpose of reducing or preventing fuel injection system or intake valve deposits, and that is not intentionally removed prior to the gasoline's sale or use.

(2) "Bulk purchaser-consumer" means a person who purchases or otherwise obtains gasoline in bulk and then dispenses it into the fuel tanks of motor vehicles owned or operated by the person.

(3) "California gasoline" means gasoline sold or intended for sale as a motor vehicle fuel in California.

(4) "Chemical composition" means the name, percentage by weight, and chemical identification of each compound in an additive.

(5) "Distributor" means any person who transports or stores or causes the transportation or storage of gasoline, produced or imported by another person, at any point between any producer's or importer's facility and any retail outlet or wholesale purchaser-consumer's facility.

(6) "Final distribution facility" means the stationary gasoline transfer point from which gasoline is transferred into the cargo tank truck, pipeline, or other delivery vessel from which the gasoline will be delivered to the facility at which the gasoline will be dispensed into motor vehicles.

(7) "Gasoline" means any fuel which is sold or intended for sale as a California motor vehicle fuel and is either: (a) commonly or commercially known or sold as gasoline, or (b) any fuel blend of gasoline as defined in (a) and alcohol in which the portion of gasoline is more than 50 percent of the total blend.

(8) "Gasoline production facility" means a facility in California at which gasoline is produced; it does not include a facility whose sole operation is to transfer gasoline or to blend additives into gasoline.

(9) "Importer" means any person who first accepts delivery of gasoline in California.

(10) "Import facility" means the facility at which imported gasoline is first received in California, including, in the case of gasoline imported by cargo tank and delivered directly to a facility for dispensing gasoline into motor vehicles, the cargo tank in which the gasoline is imported.

(11) "Motor vehicle" has the same meaning as defined in section 415 of the Vehicle Code.

(12) "Produce" means to convert liquid compounds which are not gasoline into gasoline.

(13) "Producer" means any person who produces California gasoline in California.

(14) "Retail outlet" means any establishment at which gasoline is sold or offered for sale for use in motor vehicles.

(15) "Supply" means to provide or transfer a product to a physically separate facility, vehicle, or transportation system.

(c) Certification Requirements.

(1)(A) No gasoline formulation shall be certified under this subsection (c) unless the applicant for certification demonstrates each of the following to the executive officer's satisfaction:

(i) The gasoline formulation meets ~~the unlimited mileage standard of a maximum of 10050 milligrams averaged over all intake valves when tested in accordance with ASTM D 5500-948, which is incorporated herein by reference, with modifications noted in sections (D)(IV)(8.5.5.1) and (8.7.1.1) of the Stationary Source Division's Test Method for Evaluating Intake Valve and Combustion Chamber Deposits in Motor Vehicles, dated [insert date of adoption] July 2, 1996, which is also incorporated herein by reference. As an alternative, intake valve deposits may be tested in accordance with subsection (c)(1)(A)(iii).~~

(ii) The gasoline formulation does not result in a flow loss of more than five percent for any fuel injector when tested in accordance with ASTM D 5598-945a, which is incorporated herein by reference.

(iii) The gasoline formulation *meeting the requirements of (c)(1)(A)(i), does not result in more than 1300 milligrams total deposit weight, averaged over all four combustion chambers is capable of reducing fuel injector deposits so that no fuel injector suffers a flow loss of more than five percent, or, does not result in more than 140 percent total deposit weight from all four combustion chambers, relative to the gasoline formulation containing no additive*, when tested in accordance with the Stationary Source Division's Test Method for Evaluating *Intake Valve and Combustion Chamber Port-Fuel Injector Deposits in Vehicle Engines*, dated **[insert date of adoption] July 2, 1996**, which is incorporated herein by reference.

(B) The executive officer may approve alternative test procedures for demonstrating satisfaction with any of the performance criteria set forth in subsection (c)(1)(A) if an applicant or potential applicant demonstrates to the executive officer's satisfaction that a gasoline formulation which meets the performance criteria of the alternative test procedure would also meet the performance criteria specified in subsection (c)(1)(A).

(2) Any producer, importer, or distributor may apply to the executive officer for certification of a gasoline formulation in accordance with this subsection (c). The application shall be in writing and shall include, at a minimum, the following:

(A) The name and chemical composition of the additive or additives in the gasoline formulation, except that if the chemical composition is not known to either the applicant or to the manufacturer of the additive (if other than the applicant), the applicant may provide a full disclosure of the chemical process of manufacture of the additive in lieu of its chemical composition.

(B) The minimum concentration of each additive in the gasoline formulation in terms of gallons of additive per thousand gallons of gasoline.

(C) The results of tests conducted on the gasoline formulation pursuant to the test procedures set forth in subsection (c)(1), all data generated by the tests, the identity of the entity which conducted each test, and a description of the quality assurance and quality

control procedures used during the testing.

(D) Data demonstrating that the fuel used for certification testing ("certification test fuel") is representative of the gasoline formulation for which certification is requested. Properties of the certification test fuel must be at least 80 percent of the maximum properties of the gasoline formulation to be certified for the following: aromatic hydrocarbon content, olefin content, sulfur content, and oxygen content. *The T90 distillation temperature of the certification test fuel cannot be less than 40 °F below the gasoline formulation for which certification is requested* All other certification test fuel properties must be representative of typical commercial gasoline.

(E) Data demonstrating ~~that~~ how the certification test fuel will be produced ~~from~~ including a list of blend stocks, such as reformate, oxygenates, cracked stocks, alkylate, isomerate, straight run stocks and any other blend stocks, along with the percentage of the total which each blend stock comprises. Data may also be requested which demonstrates that the certification test fuel blend stocks are representative of typical California refinery blend stocks used for the production of California gasoline.

(F) The theoretical mechanism of action (if known) of the additive in meeting any of the performance criteria set forth in subsection (c)(1)(A).

(G) Copies of all material pertaining to the additive or additives in the gasoline formulation, submitted by the applicant to the U.S. Environmental Protection Agency pursuant to 40 CFR sections 79.6, 79.10 and 79.11. If the applicant has submitted no such material, copies of all material pertaining to the additive or additives in the gasoline formulation, submitted by the additive manufacturer to the U. S. Environmental Protection Agency pursuant to 40 CFR sections 79.6, 79.20 and 79.21.

(H) A test method reasonably adequate for determining the presence and concentration of each additive in the gasoline, including test method reproducibility. The test method may involve identification of the presence of a surrogate marker substance if the applicant demonstrates that such test method will adequately demonstrate the presence and concentration of the additive.

(3) Within 30 days of receipt of an application, the executive officer shall advise the applicant in writing either that it is complete or that specified additional information is required to make it complete. Within 30 days of submittal of additional information, the executive officer shall advise the applicant in writing either that the application is complete, or that specified additional information or testing is still required before it can be deemed complete.

(4) If the executive officer finds that an application meets the requirements of this section and determines that the applicant has satisfactorily made the demonstrations identified in subsection (c)(1), then he or she shall issue an Executive Order certifying the gasoline fuel formulation. The executive officer shall act on a complete application within 30 days after the application is deemed complete.

(5) If the executive officer determines that the gasoline sold by a producer, importer or distributor contains the minimum concentration of additives identified in an applicable certification, but substantially fails to meet the performance criteria set forth in subsection (c)(1), the executive officer shall revoke or modify the prior certification as is

necessary to assure that gasoline sold by the producer, importer or distributor meets the performance criteria set forth in subsection (c)(1). The executive officer shall not revoke or modify a prior certification order without first affording the applicant for the certification an opportunity for a hearing in accordance with title 17, California Code of Regulations, part III, chapter 1, subchapter 1, article 4 (commencing with section 60040). If the executive officer determines that a producer, importer or distributor would be unable to comply with this regulation as a direct result of a certification revocation or modification pursuant to this subsection, the executive officer may delay the effective date of such revocation or modification for such period of time as is necessary to permit the person to come into compliance in the exercise of all reasonable diligence.

(d) Recordkeeping.

(1) Each producer, importer, and distributor who has been issued a certification pursuant to subsection (c) must maintain records identifying each facility at which he or she adds an additive to California gasoline in order to comply with subsection (a)(1). For each such facility, the producer, importer or distributor must compile records showing on a monthly basis for each grade of gasoline:

[i] the volume of California gasoline supplied from the facility by the producer, importer or distributor,

[ii] the volume of California gasoline to which the producer, importer or distributor added the additive to comply with subsection (a)(1), and

[iii] the name and volume of each additive (or additive package) added to the California gasoline fuel. Records covering a month must be compiled no later than 30 days after the end of the month, and must be retained for at least two years after the end of the month.

(2) Any person required by subsection (d)(1) to compile and retain records must provide to the executive officer any such records within 20 days of a written request received from the executive officer or her/her designee before expiration of the period during which the records are required to be retained. Whenever such a person fails to provide records regarding a volume of California gasoline in accordance with this subsection (d)(2), the volume of California gasoline will be presumed to have been sold by the person in violation of subsection (a)(1).

Note: Authority cited: Sections 39600, 39601, 43013, 43018, and 43101 of the Health and Safety Code, and *Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District*, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975). Reference: Sections 39000, 39001, 39002, 39003, 39500, 39515, 39516, 41511, 43000, 43016, 43018, and 43101, Health and Safety Code, and *Western Oil and Gas Ass'n. v. Orange County Air Pollution Control District*, 14 Cal.3d 411, 121 Cal.Rptr. 249 (1975).

## APPENDIX B

### **STAFF EVALUATION OF COMBUSTION CHAMBER DEPOSITS**

## **APPENDIX B**

### **STAFF EVALUATION OF COMBUSTION CHAMBER DEPOSITS**

This appendix provides a comprehensive discussion of the staff's evaluation on combustion chamber deposits that supports the proposed new combustion chamber deposit performance demonstration for gasoline certification. Included are discussions on combustion chamber deposit formation, combustion chamber deposit impacts and benefits of controlling combustion chamber deposits.

#### **A. *Overview***

In November 1993, the Coordinating Research Council (CRC), an organization representing the research interests of auto and oil industries, conducted a major workshop to determine the status of combustion chamber deposits. At that workshop, the Chrysler Corporation, and other automobile manufacturers, indicated that customer complaints of a "knocking noise" led them to evaluate combustion chamber deposits and their impacts on driveability. Automakers found that some engine designs were sensitive to combustion chamber deposit formation and led to a condition where deposits on the piston top and cylinder head would cause the piston head to rock at top dead center, and thereby cause a knocking sound, known as "carbon rap". Since the early 1990s, combustion chamber deposits have been extensively studied to gain a better understanding of the principles of formation, deposit morphology, the emission effects, and effect on octane requirement increase.

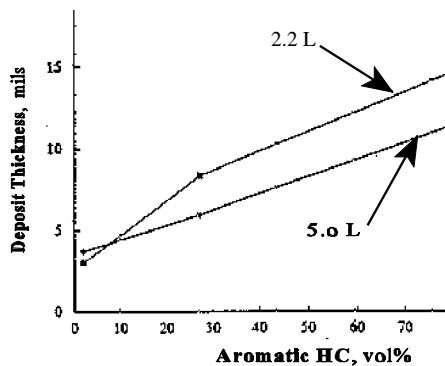
Over the past few years, the staff also received some data from additive companies suggesting that significant emission reductions were possible through combustion chamber deposit control. This prompted the staff to conduct a comprehensive evaluation of combustion chamber deposits and their impact on vehicle emissions. The evaluation has involved the review of available information and research on combustion chamber deposits. Several studies published by the Society of Automotive Engineers (SAE) were reviewed by the staff, as well as data from individual company combustion chamber deposit studies. Numerous meetings were conducted to solicit information. The CRC also presented findings from their recent study on combustion chamber deposits.

The staff found that the total amount of combustion chamber deposit formation for a given vehicle varies significantly due to the effects of driving cycle, gasoline properties, engine design, oil consumption, gasoline deposit control additive types, and dosage of gasoline additives used. The low speed and low load driving condition was found to be the most severe condition for combustion chamber deposit formation. Whereas, the high speed and high load driving condition was identified as the least severe.

Essentially, combustion chamber deposits form as a result of the thermal decomposition of heavy hydrocarbon components mainly within the base gasoline and the deposit control additive package. Studies have demonstrated a correlation between the aromatic hydrocarbon content of gasoline and the amount of combustion chamber deposits that will be formed in an engine.

In one combustion chamber deposit study published by SAE, Texaco found a clear correlation between aromatic hydrocarbon (HC) content and combustion chamber deposit

**Figure B-1**  
Combustion Chamber Deposit  
Thickness vs. Aromatics



Source: SAE 932812

formation. They also linked the aromatic HC content to the chemical molecular structure of combustion chamber deposits. For this study, Texaco operated two 1985 2.2L PFI Turbo engines and two 1989 5.0L SPFI engines on a dynamometer over a pre-described driving cycle. Three test fuels consisted of an alkylate (3.7vol percent aromatics), an unleaded regular (27vol percent aromatics), and a reformat (86.7vol percent aromatics). Figure B-1 shows the combustion chamber deposit thickness results for both vehicle models. The graph shows a clear change in combustion chamber deposit level with increasing aromatic HC content in the fuel.

Engine oils and engine oil additives also have been shown to contribute to a lesser degree to combustion chamber deposit formation. Lab tests reveal that combustion chamber deposit formation is a thermally dependent occurrence and is greatly influenced by the thermal stability of the gasoline and deposit control additive package. Increases in gasoline T90 distillation temperature, multi-ring aromatic hydrocarbon content and olefin content also increases combustion chamber deposit formation.

Physically, combustion chamber deposits appear to be amorphous and contain a sometimes shiny deposit base layer with another surface deposit layer characterized by a porous aromatic carbon composition. In the study discussed above, Texaco conducted <sup>13</sup>C nuclear magnetic resonance (NMR) to find that combustion chamber deposits consisted of an aromatic carbon backbone. Texaco also found that as aromatic HC content was increased, the molecular structure of the combustion chamber deposit changed to include a higher degree of polymerization and less oxidation.

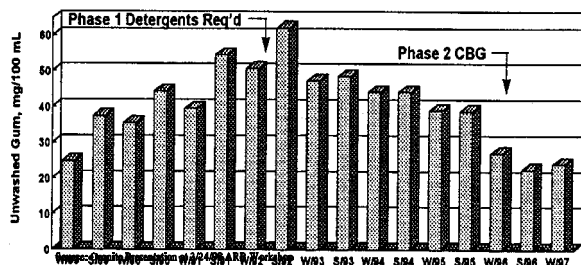
As a result of a General Motors study, data indicates that the initial stage of combustion chamber deposit formation occurs as gasoline hydrocarbon molecules partially oxidize and condense onto metal surfaces of the piston top, intake valve face and cylinder head. Deposits then undergo pyrolysis or polymerization and creates a high tension liquid. As deposits continue to form, the surface undergoes further thermal degradation to produce

another distinct layer of deposits composed of a dry low density crust. Surface deposits eventually erode under the physical stresses present in the cylinder during the combustion process. Deposit formation is a dynamic process where new deposits form during combustion, while others erode. Other studies show that long term combustion chamber deposit equilibrium is typically reached after about 10,000 miles of accumulation.

## B. Additive Contribution to Combustion Chamber Deposits

It has been well established that deposit control additive chemistry and dose rate act as major contributors to combustion chamber deposit formation. The automobile industry found that combustion chamber deposits were the cause of carbon rap. Figure B-2 was presented by the Oronite Additive Company at the ARB March 24<sup>th</sup> workshop, to show that California gasoline unwashed gum level rose dramatically during the early 1990's. Unwashed gum measurements are routinely used by industry to determine the overall amount of additives in a base gasoline. The increase in unwashed gum, coincided with implementation of the California

**Figure B-2**  
Unwashed Gum- AAMA National Survey  
Premium Gasoline- SF and LA Sample Average



deposit control additive program. Also, the peak in gasoline unwashed gum level occurred in the summer of 1992, which also coincided with Chrysler's reports of carbon rap. Figure B-2 also shows a dramatic reduction in the unwashed gum level after the introduction of CaRFG in June of 1996. Since June 1996, it appears that the unwashed gum level of commercial gasolines have reduced slightly more and may have reached an equilibrium.

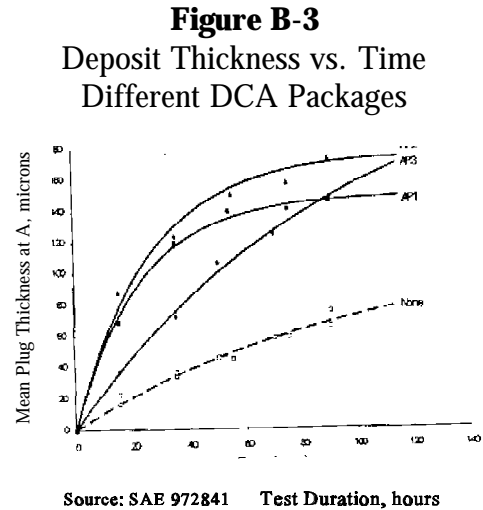
In a study to determine the effect of fuels and additives on combustion chamber deposit growth rates, Shell Research Limited conducted a series of experiments using a modified four cylinder 1.8L Volkswagen (VW). The VW engine was retrofitted to contain removable plugs which were exposed to the combustion chamber. The plugs were then fitted with small metal coupons which were then removed to obtain combustion chamber deposit thickness and weight measurements. This same technique has been used by Ford and others to study combustion chamber deposits.

Figure B-3 shows combustion chamber deposit thickness results for an untreated base fuel, and for three additives, added to the same base fuel. Testing continued for 120



hours and the plugs were periodically removed and measured. The gasoline used for this experiment was a commercial unleaded blend with a T90 of 329 °F, aromatics content of 57 volume percent, olefins content of 4 volume percent, sulfur content of 123 ppmw, and an unwashed gum level of 14 mg/100ml. The three additives all demonstrated good intake valve deposit performance in earlier tests.

The first additive, identified as AP1, contained a polyisobutylene succinimide detergent with a carrier oil. The second additive, identified as AP2, was comprised of a polyisobutylene amine (PIBA) detergent with a carrier oil. While the third additive, identified as AP3, was totally synthetic and was comprised of a polyether amine (PEA) detergent. As the figure indicates, the combustion chamber deposit level increases dramatically above the base fuel level because of the additives used. The results also indicate that gasolines containing additive, eventually reach a stabilized equilibrium. Untreated base fuels require a much longer period of time to reach equilibrium. However, the presence of additives significantly reduces the time required to reach equilibrium. Figure B-3 also points out that additive chemistries influence the long term equilibrium level. However, based on the results of this study, it appears that in the long run, additives may perform to produce combustion chamber deposits within a defined range. Several other studies have been conducted to document the impact of additive packages on combustion chamber deposits.

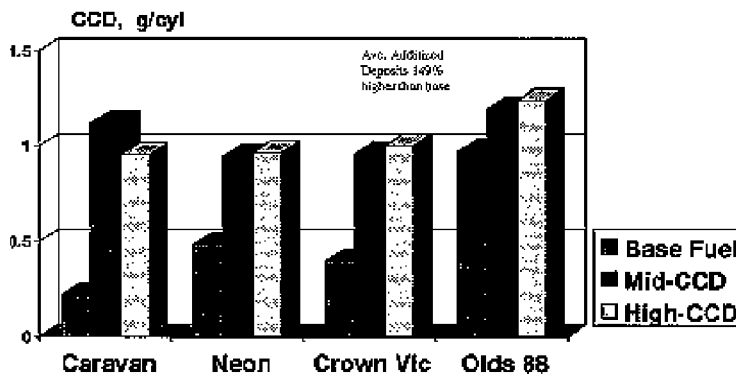


The Ethyl Corporation conducted a 25,000 mile fleet test using 25 2.3L Ford Rangers. Some vehicles were tested on untreated base fuels, while others were tested on three different commercial deposit control additive packages. The fuels used was representative of federal reformulated gasoline and the three deposit control additive packages used included a PEA with no carrier fluid, a PIBA with mineral oil carrier, and a PIBA with a synthetic carrier. All three deposit control additive packages were commercially available products. Ethyl found that the use of commercial deposit control additive packages increased base fuel combustion chamber deposits mass by as much as 28-40 percent, depending on deposit control additive chemistry. The test also indicated the lowest combustion chamber deposit measurement for the PEA detergent. The high combustion chamber deposit measurement was produced from the PIBA with mineral oil carrier additive package.

In 1995, the CRC also conducted a major research study to assess combustion chamber deposits. Under the study, the CRC tested four vehicle types (Caravan, Neon, Crown Victoria, and Olds 88) to assess the emission impacts of combustion chamber

deposits. Two deposit control additive packages were selected which were anticipated to give moderate and high combustion chamber deposit levels. However, the additive packages resulted in similar elevated combustion chamber deposit levels. Figure B-4 shows the test results. As shown, the combustion chamber deposit level increased dramatically due to deposit control additives. The study found that while individual results varied by vehicle model, the overall fleet average experienced about a 40 percent increase in combustion chamber deposits over the base fuel with no deposit control additives.

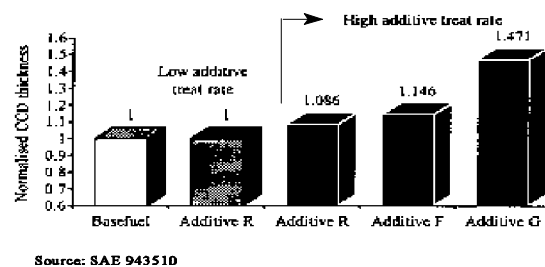
**Figure B-4**  
CRC Study Combustion Chamber Deposit Levels



Additive G was a combination of polybutene amine detergent with neutral oil. After mileage accumulation, engine combustion chamber deposits were measured using a Fischer Dual Scope MP4 nonferrous deposit thickness probe. Other studies have shown that combustion chamber deposit thickness measurements correlate well with combustion chamber deposit mass measurements.

Figure B-5 shows that deposit control additive chemistry affects combustion chamber deposit formation. The worst deposit control additive package, additive G, resulted in 47 percent thicker combustion chamber deposits relative to the untreated base fuel, whereas the succinimide/PEA additive package contributed to a nine percent increase in thickness when tested with a heavy dose rate.

**Figure B-5**  
The Effect of Additive Chemistry on Combustion Chamber Deposit Thickness



However, most studies on commercial fuels indicated that typical deposit control additive packages can contribute 20 to 40 percent more combustion chamber deposits above the base fuel.

### ***C. Combustion Chamber Deposit Emission Impact***

Studies to determine emission impacts of combustion chamber deposits show that hydrocarbon (HC) and carbon monoxide (CO) emissions do not correlate well with combustion chamber deposit formation. Some researchers believe that combustion chamber deposits may act as a sponge to trap gasoline HC molecules within the porous surface, and subsequently release them during the exhaust stroke. This condition would increase engine out HC emissions. However, most studies lead to no clear correlation for either CO or HC emissions.

Studies have established that combustion chamber deposits act as insulators in the combustion chamber, thereby affecting the combustion process temperature. It is believed that combustion chamber deposits store heat from the combustion process to elevate the in-cylinder temperature. The increased temperature in the cylinder causes NO<sub>x</sub> emissions to increase. Emission degradation from aging vehicles is a well established fact and the ARB includes vehicle deterioration factors in emissions inventory modeling efforts.

Several studies have been conducted to verify the NO<sub>x</sub> effect from combustion chamber deposits. Typically, these studies utilize new or clean engines which are operated on test fuels and additives. Baseline NO<sub>x</sub> emissions are determined through testing prior to mileage accumulation. After mileage accumulation, emission tests are repeated. Then the engine is dismantled and combustion chamber deposits are manually removed from the engine. After mechanical removal, emission tests are repeated to determine how the emissions change.

Table B-1 show the results of several studies which were conducted on a wide variety of vehicles, gasoline formulations, and additives. Most studies were performed on gasolines representative of typical national gasoline. In all studies, NO<sub>x</sub> emissions were reduced in response to combustion chamber deposit removal. The range of NO<sub>x</sub> reduction results were 12 to 55 percent, with an average of about 25 percent. These findings indicate a clear downward NO<sub>x</sub> emissions trend with significant combustion chamber deposit removal.

The studies in Table B-1 determined the NO<sub>x</sub> impact of removing combustion chamber deposits from a dirty engine to determine the overall combustion chamber deposit/NO<sub>x</sub> relationship. However, only limited data was available for the staff's evaluation to determine the potential emissions benefit of small incremental combustion chamber deposit

removal. The staff has been informed that the CRC plans to conduct another major national study to determine the emission impacts of incremental combustion chamber deposit reduction.

**Table B-1**  
Summary of Combustion Chamber Deposit  
Clean-up Studies

<u>Company</u>	<u>NOx Reduction</u>	<u>Source</u>
Texaco	12-39%	SAE 940345
Penn State	30%	SAE 950740
Oronite	15-55%	fleet test
Shell	25%	SAE 962027
Toyota	20%	SAE 941893
CRC Study	19.6%	fleet test
Nippon Oil	30%	SAE 971721

The staff expects that the equilibrium level of combustion chamber deposits in the California vehicle fleet is lower and within a more limited range than the national combustion chamber deposit level. This is because CaRFG regulations result in commercial gasolines which are within an expected property range and would likely produce combustion chamber deposits within a narrower range. The use of improved deposit control additive packages would further reduce the variability of combustion chamber deposit contribution among deposit control additive packages. Thus, we would expect that the NOx reductions from completely removing combustion chamber deposits, would be lower for the California vehicle fleet.

#### ***D. Reduced Combustion Chamber Deposit Level in California***

With the adoption of the CaRFG regulations, eight different properties of gasoline were specified. Because of the reformulation, gasoline was made to be much less deposit forming. The gasoline properties of T90 distillation temperature, olefin hydrocarbon content and aromatic hydrocarbon content were significantly reduced under the CaRFG regulations. Table B-2 shows that the olefin content of gasoline was reduced from 9.2 volume percent to 3.9 volume percent, and aromatic hydrocarbon of gasoline was reduced from 32 to 23 volume percent. Based on Figure B-1, which shows the correlation between gasoline aromatic content and combustion chamber deposit mass, a reduction from 32 to 23 of aromatic content would translate to about 23 percent decrease in combustion chamber deposit mass just due to the gasoline property effect.

Introduction of CaRFG resulted in the T90 distillation temperature of gasoline being reduced from 329 °F to about 300 °F. This is a significant change since the amount of combustion chamber deposit formation is dependent upon the amount of the heavy components within gasoline (components typically associated with the T90 property) and the chemistry of the deposit control additive packages.

**Table B-2**  
Comparison of Fuel Properties

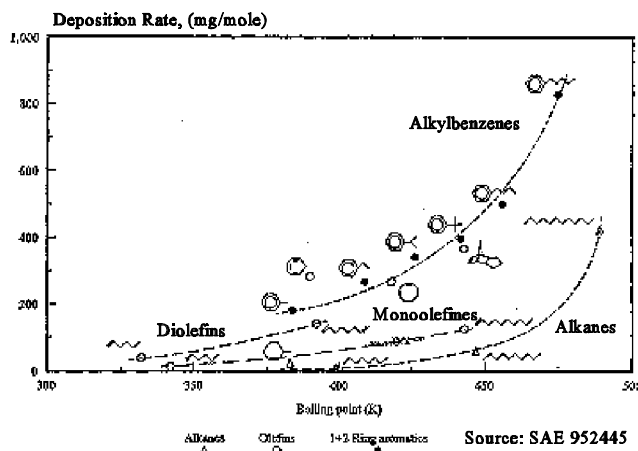
<b><u>Property</u></b>	<b><u>Pre-CaRFG<sup>a/</sup></u></b>	<b><u>Avg. CaRFG<sup>b/</sup></u></b>
T90, °F	329	302
T <sub>50</sub> , °F	212	197
Aromatic HC,	32	23
Benzene, vol%	2	0.55
Olefin HC, Vol%	9.2	3.9
Oxygen, wt%	0	2.07
Sulfur, ppmw	150	20
RVP, psi	7.8	7.0

<sup>a/</sup> ARB Gasoline Survey; TSD on Phase for CaRFG, dated October 4, 1991

<sup>b/</sup> 1998 ARB Gasoline survey

In a 1995 SAE paper, Shell reported the results of a study which determined a correlation between experimentally derived combustion chamber deposit formation rates and hydrocarbon boiling point. For this experiment, Shell devised a “quench chamber” apparatus, which simulates the same chemical reactions evident during combustion chamber deposit formation in an engine. Several hydrocarbon streams of various chemical structure (i.e. alkanes, mono and di-olefins, alkyl substituted aromatics) were used to form deposits in the quench chamber and the formation rates were measured. Figure B-6 shows the quench chamber formation rates for various hydrocarbon types, by boiling point. With a reduction in T90 from 329 °F (438 °K) to 302 °F (423 °K), Figure B-6 would indicate a dramatic elimination of olefin and multi-ring aromatic precursors within the full boiling range of gasoline.

**Figure B-6**  
Correlation Between Hydrocarbon Boiling Point  
& Combustion Chamber Deposit Formation



Another major change to gasoline under CaRFG relates to the mandated use of oxygenates. In California, the oxygenate of choice has been methyl tertiary butyl ether (MTBE). Vehicle studies conducted by Ford and others, indicate that the use of MTBE results in significantly lower combustion chamber deposit levels, relative to base gasolines with no MTBE. Because MTBE is a partially oxygenated compound with a relatively low boiling point, MTBE is expected to fully decompose in the combustion chamber and leave no deposits.

Therefore, researchers theorize that

the dilution effects of MTBE in gasoline blends contribute to lower combustion chamber deposit levels.

Another significant evolution which has led to reduced combustion chamber deposits since 1992, relates to the use of improved deposit control additive packages. The staff's review of gasoline certifications revealed that deposit control additive packages have evolved to be more effective, and require less dosage. Table B-3 shows a comparison of deposit control additive packages which were approved for use in gasoline in 1992 and 1996. In 1992, deposit control additive packages consisted mainly of polyolefin amine (POA) detergents with mineral oil based carrier fluids. These deposit control additives also required higher dosage rates to meet the gasoline certification performance standards. The staff found that in 1992, deposit control additives required an average dose rate of 279 pounds of additive per thousand barrels of gasoline (ptb).

By 1996, most additive packages consisted of synthetic carrier fluids and contained improved polyisobutylene and polyether amine detergents. At the same time, CaRFG was introduced into the market which lowered the base fuel contribution to deposits. By 1996, the average deposit control additive dose rate had been reduced to 127 ptb.

**Table B-3**  
Comparison of Deposit Control Additive Packages

Addit. Pkg.	1992		Addit. Pkg.	1996	
	Detergent <sup>a/</sup>	Carrier		Detergent <sup>a/</sup>	Carrier
A	POA	Mineral Oil	I	POA	Mineral Oil
B	PEA	none	J	PIBA	Mineral Oil
C	PIBA	Synthetic	K	PEA	Synthetic
D	POA	Mineral Oil	L	PEA/PIBA	Synthetic
E	PIBA/PES	Mineral Oil	M	PIBA	Synthetic
F	POA	Mineral Oil	N	PEA/POA	none
G	POA	Mineral Oil	O	PEA	none
H	POA	Mineral Oil	P	PIBA	Synthetic

<sup>a/</sup> POA- Polyolefin Amine; PEA- Polyether Amine; PIBA- Polyisobutylene Amine  
PES- Polyether Succinimide;

In 1996, Chevron reported findings from their four vehicle study which indicated that on average, a prototype CaRFG test gasoline produced about 50 percent less combustion chamber deposits relative to federal commercial gasolines. Chevron also performed a separate competitor survey using three vehicle models (3.3L Intrepid, 2.3L Achieva, 2.3L Ranger) and various commercial gasolines containing deposit control additive packages. Three of the test fuels were CaRFGs and six were federal commercial gasolines. Chevron found that for this study, CaRFG produced about 30 percent less combustion chamber deposit mass relative to federal commercial gasolines, which were similar to pre-CaRFG.

***E. Effect of Reduced California Combustion Chamber Deposit Level***

The staff has discussed that in 1992, additive packages were not optimized and gasoline was more deposit forming than after 1996. Studies conducted on pre-CaRFG type test gasolines indicate that on average, the pre-CaRFG combustion chamber deposit level was about 1555 mg/cylinder. This value is based on the average of all testing across various test gasolines and test vehicles (see Appendix C for more details).

The staff has also shown that improvements in additive effectiveness and in gasoline properties have led to a significant reduction in the California vehicle fleet combustion chamber deposit equilibrium level. Studies conducted on CaRFG type test gasolines

indicate that on average, CaRFG forms about 1168 mg/cylinder. Again, this value is based on the average of tests across various test gasolines and test vehicles (see Appendix C). Therefore, based on this data, the staff estimates that the average combustion chamber deposit level has been reduced by about 380 mg/cylinder within the California vehicle fleet. This value compares to the result of Chevron's competitor survey which found that on average, CaRFG combustion chamber deposit mass was about 430 mg/cylinder less than comparative pre-CaRFG type test gasolines.

The staff also cited several studies showing the dramatic reduction in NO<sub>x</sub> emissions when combustion chamber deposits are completely removed from an engine (see Table B-1). The CRC combustion chamber deposit study found a 19.6 percent reduction in NO<sub>x</sub> after cleaning up combustion chamber deposits from the engine. While the staff recognizes that this correlation is based on complete removal of combustion chamber deposits, the use of this correlation should still provide a reasonable measure of NO<sub>x</sub> reductions due to the large scale combustion chamber deposit reduction under CaRFG.

Therefore, based on these findings, the staff estimates that at least a five percent reduction in NO<sub>x</sub> emissions are a result of the reduction in the equilibrium combustion chamber deposit level from vehicles running on pre-CaRFG, to the lower combustion chamber deposit equilibrium level of the same vehicles running on CaRFG. For 1996, this NO<sub>x</sub> reduction in vehicle emissions equates to an approximate 50 tons per day reduction in the vehicle emission inventory. The staff has prepared a separate detailed analysis of the estimated NO<sub>x</sub> reduction. This analysis is contained in Appendix C of this report.

#### ***F. Determination of Proposed Combustion Chamber Deposit Performance Standard***

The staff developed the proposed combustion chamber deposit performance standard based on determining a maximum combustion chamber deposit level expected from CaRFG. Table B-4 contains a summary of the combustion chamber deposit vehicle test data for CaRFG compiled by the staff. The range in test results are shown separately for 10,000 mile tests on the BMW 318i vehicle (currently required for intake valve deposit testing). Other data shown were taken from several studies spanning a wide variety of engine types, gasoline additives, and test duration. For comparison, the staff also included limited data from combustion chamber deposit tests on laboratory bench engines. In evaluating the data, the staff believes that it is not appropriate to consider results for combustion chamber deposit tests less than 10,000 miles. Several studies show that short term tests may not accurately account for long term combustion chamber deposit equilibrium levels. A complete list of publicly available combustion chamber deposit data for CaRFG is shown in Appendix C.

To determine the maximum combustion chamber deposit "cap" performance standard being proposed, the staff reviewed all available combustion chamber deposit data



for CaRFG. For non-BMW vehicles, the combustion chamber deposit test results ranged within 898 to 1582 mg/cylinder, with an average of about 1168 mg/cyl. However, the staff believes that it is more appropriate to determine the combustion chamber deposit performance standard using data derived from the same BMW vehicle which is being proposed for use under the new ARB combustion chamber deposit vehicle test method. For the BMW, Table B-4 shows a range of 1015 to 1171 mg/cyl for additized CaRFG and 682 to 925 mg/cyl for unadditized CaRFG.

**Table B-4**  
Combustion Chamber Deposit Test Results  
for CaRFG

	<u><b>mg/cylinder</b></u>
<b><u>BMW Vehicle Data</u></b>	
- <i>CaRFG (no additive)</i>	682 - 925
- <i>CaRFG (with additive)</i>	1015 - 1171
<b><u>Non BMW Vehicle Data</u></b>	838 - 1582
<b><u>Bench Test Data</u></b>	690-1250

To derive the proposed 1300 mg/cyl standard, the staff used test data for unadditized CaRFG from Table B-4. Then the staff applied an estimated maximum incremental deposit control additive contribution of 40 percent above base fuel. As discussed earlier, studies on commercial gasolines indicated that commercial additives typically contribute 20 to 40 percent more combustion chamber deposits above the base gasoline with no additive present. Therefore, by multiplying the 925 mg/cyl combustion chamber deposit level by 40 percent, the staff estimated the maximum California combustion chamber deposit level from the BMW vehicle. The 1300 mg/cyl standard is the sum of the maximum demonstrated combustion chamber deposit level and the estimated maximum deposit control additive package contribution above CaRFG. Therefore,

$$\begin{aligned}
 &925 \text{ (mg/cyl)} \times 40\% = 370 \text{ (mg/cyl)} \\
 \text{thus, California combustion chamber deposit cap max.} &= 925 \text{ (mg/cyl)} + 370 \text{ (mg/cyl)} \\
 &= 1295 \text{ mg/cyl, or } \underline{\underline{1300 \text{ mg/cyl}}}
 \end{aligned}$$

## **APPENDIX C**

### **NO<sub>x</sub> BENEFIT CALCULATION**

## APPENDIX C

### NO<sub>x</sub> BENEFIT CALCULATION

#### Introduction

With the introduction of CaRFG and the improvement of deposit control additive formulations, the combustion chamber deposit level in gasoline vehicles has decreased from the early 90's. The reduction is due in part to the lower aromatics content and lower T90 specification for cleaner burning gasoline and in part to the reformulation of gasoline additives. Gasoline additives today contain components that cause less combustion chamber deposits than earlier formulations. By estimating the reduction in the combustion chamber deposit level between pre-CaRFG and CaRFG, staff was able to estimate the NO<sub>x</sub> benefit by using a correlation derived from the CRC combustion chamber deposit emission study.

#### Discussion of Combustion Chamber Deposit Data

To determine the change in combustion chamber deposits, the deposit level for pre-CaRFG in 1992 gasoline was compared with the CaRFG deposit level in 1997 gasoline. Table C-1 shows that the properties of pre-CaRFG is similar to federal conventional and unoxygenated federal 65<sup>th</sup> percentile fuel. The levels of aromatic HC and olefin HC, and the T90 specifications are similar. Tables C-2 and C-3 contain combustion chamber deposit test data results using gasoline similar to pre-CaRFG and CaRFG. From these results, the average combustion chamber deposit level from the use of pre-CaRFG and CaRFG were estimated to be 1555 and 1168 mg/cyl, respectively.

#### Discussion of NO<sub>x</sub>/Combustion Chamber Deposit Correlation

To determine the impact of lower combustion chamber deposits due to CaRFG, staff calculated a factor representing the percent reduction in NO<sub>x</sub> emissions per gram of combustion chamber deposits removed from the engine. Staff used test data from the CRC combustion chamber deposit study to derive this factor (see Fig. B-4 and Table B-1). In this study, the CRC measured combustion chamber deposits and the NO<sub>x</sub> level in four different vehicle types running on high deposit forming gasolines and on a base gasoline. Based on the CRC study, this factor was calculated to be 18.5% NO<sub>x</sub> red./g combustion chamber deposits. The factor was derived by dividing the difference in NO<sub>x</sub> emissions, 19.6%, by the average amount of combustion chamber deposits removed per cylinder (i.e. 18.5% NO<sub>x</sub> red./g combustion chamber deposits = 19.6% NO<sub>x</sub> red./1.06 g combustion chamber deposits).

### Calculation of NOx Benefit

A NOx benefit was estimated from the following equation:

$$\text{NOx Benefit} = \frac{\Delta \text{ g CCD}}{\text{Pre-CaRFG vs CaRFG}} \times \frac{18.5\% \text{ NOx reduction/g CCD}}{\text{CRC CCD Study}}$$

The first term in the equation represents the difference in combustion chamber deposit formation between 1992 and 1997 gasolines, which is calculated to be 387 mg (0.387 g). The second term in the equation, 18.5%, represents the NOx reduction per change in combustion chamber deposit weight. Therefore,

$$\begin{aligned} \text{NOx reduction} &= 0.387 \text{ g CCD} \times 18.5\% \text{ NOx red./g CCD.} \\ &= 7\% \end{aligned}$$

The CRC study is a study demonstrating that the presence of combustion chamber deposits increases NOx emissions. Therefore, staff's estimate of the NOx benefit should be considered an approximation, showing at least a 5% NOx emission reduction, associated with the lower combustion chamber deposit level. A five percent reduction equates to about 50 tons of NOx emissions per day in 1996, based on the most recent version of the motor vehicle emissions inventory model (MVEI7G1.0(c)).

Future studies are needed to determine the incremental effects of combustion chamber deposits on NOx emissions. Once the incremental emission impact of partial combustion chamber deposit removal is determined, then staff's estimated NOx benefit may be updated for accuracy. Staff understands that the CRC plans to conduct such a study this year. Additional studies also need to be done using CaRFG for the test fuel in order to calculate the benefits for California.

**TABLE C-1**  
Comparison of Fuels

	Pre- CaRFG(1)	CaRFG(2 )	Federal Conv(3)	Federal 65 <sup>th</sup> Percentile(4)	Federal 65 <sup>th</sup> Percentile w/ Oxy(4)
Aromatics,	32	23	28.6	31.1	28
Olefins, vol%	9.2	3.9	10.8	11.4	10
Sulfur, ppm	150	20	338	340	
Oxygen, wt%	0	2.07	--	0	3.7
Benzene, vol%	2	0.55	1.6		
T50, °F	212	197	207		
T90, °F	329	302	332	339	

<sup>1</sup> Survey by ARB staff

<sup>2</sup> From 1996 API/NPRA survey

<sup>3</sup> "Is Reformulated Gasoline a New Gasoline?" Office of Mobile Sources, EPA 420-F-95-007, 4/1/1995

<sup>4</sup> 65<sup>th</sup> Percentile Limits for National Generic Certification in the Federal Gasoline deposit Control Additive Regulation

**Table C-2**  
10K Mile Vehicle Testing for  
CCD's Using Fuel Similar  
to Pre-CaRFG

Test No.	Vehicle Type	Avg. CCD (mg/cyl)	Vol % Ethanol
1	2.3L Quad-4Achieva	1801	0
2	2.3L Quad-4Achieva	2534	0
3	2.3L Quad-4Achieva	1446	0
4	3.1L Lumina	883	0
5	3.1L Lumina	1033	0
6	3.1L Lumina	989	0
7	2.3L Ranger	1756	0
8	2.3L Ranger	2057	0
9	2.3L Ranger	1687	0
10	3.8L Regal	1728	0
11	3.8L Regal	2054	0
12	3.8L Regal	1301	0
13	1.8 L BMW	1086	10
14	1.8 L BMW	1968	10
15	1.8 L BMW	1452	0
16	1.8 L BMW	1436	10
17	1.8 L BMW	1262	0
18	1.8 L BMW	1525	0
19	1.8 L BMW	1848	10
20	1.8 L BMW	1582	10
21	1.8 L BMW	1542	0
22	1.8 L BMW	1392	0
23	1.8 L BMW	1310	0
24	1.8 L BMW	1517	10
25-27	various	1600	--
	Average:	1555	

**Table C-3**  
10K Mile Vehicle Testing for  
CCD's Using CaRFG

Test No.	Vehicle Type	Avg. CCD (mg/cyl)
1	1.8L BMW	1165
2	1.8L BMW	1171
3	1.8L BMW	1015
4	2.3L Achieva	898
5	2.3L Achieva	1024
6	2.3L Achieva	1463
7	3.3L Intrepid	1215
8	3.3L Intrepid	1045
9	3.3L Intrepid	1157
10	2.3L Ranger	1582
11	2.3L Ranger	1250
12	2.3L Ranger	1036
	Average:	1168

## **APPENDIX D**

### **ARB VEHICLE TEST PROCEDURE FOR EVALUATING INTAKE VALVE DEPOSITS AND COMBUSTION CHAMBER DEPOSITS**



**STATE OF CALIFORNIA  
AIR RESOURCES BOARD  
STATIONARY SOURCE DIVISION**

*[insert date of adoption]*

**TEST METHOD FOR EVALUATING FORMATION OF INTAKE VALVE AND  
COMBUSTION CHAMBER DEPOSITS IN MOTOR VEHICLES**

STATE OF CALIFORNIA  
AIR RESOURCES BOARD  
STATIONARY SOURCE DIVISION

*[insert date of adoption]*

TEST METHOD FOR EVALUATING FORMATION OF INTAKE VALVE AND  
COMBUSTION CHAMBER DEPOSITS IN MOTOR VEHICLES

E. PURPOSE

This test method is used to evaluate a gasoline formulation's potential to form intake valve deposits and combustion chamber deposits. The test method follows the procedure in ASTM D 5500-98 with modifications specified below to incorporate testing for combustion chamber deposits (CCDs).

F. SUMMARY OF TEST METHOD

This test method is designed to measure intake valve deposits (IVDs) and CCDs from a single vehicle test run. This test method requires following ASTM D 5500-98 for vehicle preparation and mileage accumulation. After mileage is accumulated, the cylinder head is removed and the CCDs are scraped and measured. Additional steps incorporated into the ASTM D 5500-98 have been included to provide guidance to obtain piston and cylinder head deposits. After CCD measurements are made, the intake valves are removed from the cylinder head and deposit weights are determined in accordance with ASTM D 5500-98.

G. TEST METHOD USE

This test method is to be used to measure IVDs and CCDs in the same test run. Additionally, this test method may be used to measure CCDs only.

H. TEST PROCEDURE

The provisions of ASTM D 5500-98 are incorporated into the Test Method for Evaluating Formation of Intake Valve and Combustion Chamber Deposits in Motor Vehicles with the following modifications to incorporate steps to obtain CCD weight measurements. [Note: Additions to the ASTM D 5500-98 test method are indicated in underline and deletions are indicated in ~~strikeout~~]

## 1. Scope

Refer to ASTM D 5500-98, section 1 and amend subparagraph 1.1 with the following changes:

1.1 This test method covers a vehicle test procedure for ~~evaluation~~ evaluating the formation of intake valve deposits and combustion chamber deposits (CCDs) ~~formation of~~ unleaded spark-ignition engine fuels . . . Chassis dynamometers shall not be used for this test procedure ~~as the BMW NA/SwRI IVD Test was not intended to be applicable to chassis dynamometers and since~~ no correlation between road operation and chassis dynamometers has been established for either CCD or IVD.

## 2. Referenced Documents (Refer to ASTM D 5500-98, section 2)

## 3. Terminology (Refer to ASTM D 5500-98, section 3)

## 4. Summary of Test Method

Refer to ASTM D 5500-98, section 4 and amend subparagraph 4.4 with the following changes:

4.4 After the required mileage (10.4.5) has been accumulated, the cylinder head is removed from the engine and ~~disassembled. the CCDs are scraped and removed from the piston top and cylinder head surface for each cylinder. The CCDs are then weighed. and The cylinder head is then~~ disassembled and the intake valves are weighed, visually assigned merit ratings, and photographed. Operational and mechanical criteria are then reviewed to determine if the test shall be considered valid.

## 5. Significance and Use

Refer to ASTM D 5500-98, section 5 and amend subparagraph 5.1 by adding the following:

5.1 *Test Method* — It was determined through field testing that intake valve deposits could adversely affect the driveability of certain automobiles. . .Minimizing intake valve deposits may be necessary to maintain vehicle driveability and tailpipe emissions control. It was also determined that accumulation of CCDs may cause octane requirement increase, CCD interference, and an increase in NOx emissions. This test method is based on established automotive testing laboratory test methods.

Amend subparagraph 5.1.1 with the following changes:

5.1.1 *State and Federal Legislative and Regulatory Action* — Legislative activity and rulemaking primarily by California Air Resources Board and the Environmental Protection Agency necessitate the acceptance of a standardized test method to evaluate the intake system and combustion chamber deposit forming tendency of an automotive spark-ignition engine fuel.

## 6. Apparatus (Refer to ASTM D 5500-98, section 6)

## 7. Reagents and Materials (Refer to ASTM D 5500-98, section 7)

## 8. Preparation of Apparatus

Refer to ASTM D 5500-98, section 8 and amend subparagraph 8.2.4.1 with the following changes:

8.2.4.1 Piston crowns and bore crevices shall be cleaned with a gasket scraper, fine wire brush, or

similar tools. Do not allow debris to fall into the water jacket or oil passages. Care shall be exercised so that the piston crowns and bore crevices are not damaged during cleaning. A shop-type vacuum cleaner or compressed air may shall be used to evacuate the loose carbon from the piston and piston/bore crevice.

## 9. Test Procedure

Refer to ASTM D 5500-98, section 9 and add subparagraph 9.5.1.5:

9.5.1.5 Determination of total cylinder CCD weight -- Upon removal of the cylinder head, measure the masses of IVD and CCD from the vehicle. Total cylinder CCD mass shall be reported as the sum of the deposits collected individually from the piston top, cylinder head, and intake valve face for each cylinder. Determination of piston top CCDs are contained in steps 9.5.1.5.1 through 9.5.1.5.4. Determination of cylinder head and valve face CCDs are contained in steps 9.5.1.5.5 through 9.5.1.5.9.

Add subparagraph 9.5.1.5.1:

9.5.1.5.1 With piston positioned slightly below Top-Dead-Center (TDC), scrape cylinder block deck surface with gasket scraper, and wipe with a rag. The objective is to produce a ring around each piston that tape will readily adhere to without picking up contamination. Do not use power equipment.

Add subparagraph 9.5.1.5.2:

9.5.1.5.2 A deposit collector with a smooth non-absorbent inside surface is attached to the cylinder block with a continuous seal that does not allow deposits to slide between the deposit collector and the cylinder block. The collector is designed to contain any deposits that become airborne from scraping.

Add subparagraph 9.5.1.5.3:

9.5.1.5.3 With piston at TDC, remove deposits from the piston top using stainless steel or other metal lab instruments that will not erode during use. Use a stainless steel wire brush to remove remaining deposits off the piston top. Continue brushing until all deposits are removed and only varnish remains. After scraping the piston top, move piston slightly below TDC and brush the deposits which are collected at the top of the cylinder wall into the deposit collector.

Add subparagraph 9.5.1.5.4:

9.5.1.5.4 After scraping is completed, carefully remove the deposit collector, and allow the deposits to accumulate in the deposit collector, where they can be poured into preweighed containers for piston deposit weight determination. Deposits from each piston are to be placed in individual containers.

Add subparagraph 9.5.1.5.5:

9.5.1.5.5 Remove spark plug from the cylinder to be scraped. Install a blanked off spark plug that has had its electrodes removed and been filled with solder.

Add subparagraph 9.5.1.5.6:

9.5.1.5.6 Place cylinder head on work bench with combustion chamber side facing up. Scrape off gasket material from around the combustion chambers with a gasket scraper and wipe with a rag. The objective is to produce a ring around each combustion chamber that tape will readily adhere to without picking up contamination. Do not use power equipment.

Add subparagraph 9.5.1.5.7:

9.5.1.5.7 A deposit collector that has a smooth non-absorbent inside surface is attached to the cylinder head with a continuous seal that does not allow deposits to slide between the deposit collector and the cylinder head. The collector is designed to contain any deposits that become airborne from scraping.

Add subparagraph 9.5.1.5.8:

9.5.1.5.8 Remove deposits from the combustion chamber and intake valve faces using stainless steel or other metal lab instruments that will not erode during use. As the deposits are scraped, they can be brushed into the deposit collector with a soft bristle brush. Use a stainless steel wire brush to remove remaining deposits off the combustion chamber. Continue brushing until all deposits are removed and only varnish remains.

Add subparagraph 9.5.1.5.9:

9.5.1.5.9 After scraping is completed, carefully remove the deposit collector, and allow the deposits to accumulate in the collector, where they can be poured into preweighed containers for cylinder head deposit weight determination. Deposits from each piston are to be placed in individual containers

10. Determination of Test Results (Refer to ASTM D 5500-98, section 10)

11. Final Test Report (Refer to ASTM D 5500-98, section 11)

12. Precision and Bias (Refer to ASTM D 5500-98, section 12)

13. Keywords (Refer to ASTM D 5500-98, section 13)

## **APPENDIX E**

### **CMA PETITION AND ARB RESPONSE**

(Not Available In Electronic Version)